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The Normal Density of Ammonia

BY GERHARD DIETRICHSON, LOUIS J. BIRCHER AND JOHN J. O'BRIEN

Introduction

The accompanying tabulation gives a summary of previous work in determining the density of ammonia at 0° and one atmosphere.

Blanchard and Pickering[1] in their review of the literature pertaining to gas densities conclude, in the case of ammonia, with the following statement: "The weight of a normal liter chosen is therefore 0.7710 with an uncertainty of two or three units in the last decimal place." This is exclusive of the results obtained by Leduc and of the most recent by Moles and Batuecas. In discussing the earlier work Moles and Batuecas[2] also state that they recalculated the data of Guye and Pintza, Perman and Davies and Scheuer. The resulting densities are shown in the column at the right.

The weight of a normal liter has also been calculated from the "compressibility" of ammonia, $(\partial(pv)/\partial p)_T$, using the equations

$$p_0v_0/p_1v_1 = 1 + \bar{\lambda} \qquad d_n = m/v_1 = \frac{M(1 + \bar{\lambda})}{RT_0}$$
$$p_0v_0 = m/M\,RT_0$$

where $\bar{\lambda}$ is understood to be a mean value defined as $\bar{\lambda} = \int_0^{1\text{ atm.}} \lambda\, dp$.[1] Beattie and Lawrence[3] using their own p-v-T data and the Beattie-Bridgeman equation of state

$$pv = RT + \beta/v + \gamma/v^2 + \delta/v^3$$

to obtain the p_1v_1 product, derive the value, 0.7706 g./l. On the other hand, the same form of equation applied to the data of Meyers and Jessup leads to a normal density of 0.7715 g./l.

The foregoing discloses considerable uncertainty as to the true normal density. In view of the elaborate precautions taken by the investigators in purifying ammonia from various sources, it seems certain that the irregularities are not traceable to impurities. It appears accordingly that the discrepancies must be attributed mainly to the experimental procedure adopted. All of the work up to the present has been done by either the

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(1) Blanchard and Pickering, B. S. Sci. Paper No. 529, 1926.

(2) Moles and Batuecas, *Sitzb. Akad. Wiss. Wien*, **138**, 779 (1929)

(3) Beattie and Lawrence, THIS JOURNAL, **52**, 6 (1930).

PREVIOUS WORK ON THE DENSITY OF AMMONIA

Name	Method	Source of NH_3	No. of detns.	Density	Density as recalculated by Moles and Batuecas
Leduc (1898)	Balloon	Commercial		0.7720	
Guye and Pintza (1905)	Volumeter	Commercial	5	.77083 (±0.0002)	0.7710
Perman and Davis (1906)	Volumeter	Commercial	4	.7717	
Perman and Davis (1906)	Volumeter	Commercial and $(NH_4)_2C_2O_4$	7	.77089 (±0.0004)	
Perman and Davis (1906)	Balloon	$NaNO_2$ (reduced with Al + NaOH)	4	.77090 (±0.0006)	.7714
Scheuer (1914)	Balloon	$(NH_4)_2SO_4$	16	.7708 (±0.00026)	.77093
McKelvey and Taylor[a] (1923)	Balloon and volumeter	Several sources	"Numerous"	.7713	
Meyers and Jessup[a] (1923)	Metal bombs	NH_3 prepared by McKelvey and Taylor	3	.7713 (max. var. 0.0013)	
Moles and Batuecas (1929)	Balloon	$(NH_4)_2C_2O_4$	13	.77185	
Moles and Batuecas (1929)	Balloon	Synthetic	10	.77185	
Moles and Batuecas (1929)	Balloon	Mg_3N_2	8	.77200	
				.77190	
			Adsorption correction −	.00020	
				.77170	

[a] Reported by Blanchard and Pickering.

"balloon" or the "volumeter" method. Neither of these would avoid definitely the adsorption effect expected with ammonia.

Professor F. G. Keyes proposed to the authors a number of years ago a modification of a method originally proposed and used by Maass and Russell[4] in determining the density of acetylene, methyl ether and hydrobromic acid and later by Cooper and Maass[5] in determining the density of carbon dioxide. The suggested modification provides a means of estimating quantitatively the adsorption effect on the container walls. The principle involved is that of measuring the temperature and pressure of the gas in a relatively large bulb of known volume, condensing it in a small bulb that can be sealed off and then weighing in the liquid form or under high pressure. This method obviously makes it possible to work with comparatively large amounts of material and only involves the weighing of very small bulbs with a corresponding decrease in total mass and surface area. It was assumed that the adsorption effect could be eliminated by bringing the gas down to varying final bulb pressures during the condensation process. According to the adsorption law, $q = ap^{1/n}$, the total amount adsorbed tends to approach a constant saturation value at relatively low pressures provided a true adsorption effect is involved.[6] The condensed liquid should, therefore, as the residual pressure is made progressively larger, represent material drawn from the gas phase only. By means of an approximate equation of state it is possible to calculate with exactness the small weight of gas corresponding to the residual pressure, exclusive of the adsorbed layer. This in turn when added to the weight of the gas that has been condensed would give the mass corresponding to the initial pressure. According to this procedure it becomes a matter, therefore, of determining the limiting minimum density with increasing residual pressures.

As the work progressed it was found that the method outlined above did not apparently serve to eliminate completely the adsorption effect. The authors feel, however, that this was finally accomplished by subjecting the ice-bath bulb to a thorough baking and pumping previous to the density determinations and by observing special care in removing the last traces of ammonia in the line before each condensation. The details as to this will be described more fully in a later section.

The present work was undertaken with the idea of obtaining density data at one, two-thirds and one-third of an atmosphere, also for corre-

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(4) Maass and Russell, THIS JOURNAL, **40**, 1847 (1918).

(5) Cooper and Maass, Can. J. *Res.*, **2**, 388 (1930).

(6) Keyes [Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, New York, 1916. p. 21] has called attention to the fact that ammonia very likely absorbs in the adsorbed water layer rather than adsorbing to any extent. The amount of ammonia on the walls of the globe would therefore not be related to the pressure by the above formula but more in accordance with Henry's law. In any event, however, the method will indicate the part played by the walls in retaining gas. The final outcome of our work indicates that ammonia does not adsorb on water freed surfaces.

sponding pressures at higher temperatures. At this time only the results at one atmosphere and 0° are being reported. The preliminary densities at the lower pressures and 0° were used to obtain an equation of state needed in the computation of the residual amount of gas in the bulb.

Experimental Method

The experimental work carried out divides itself into two distinct parts. The general arrangement of the apparatus for the first part, experiments Nos. 1–66, is shown in Fig. 1. That for the second, experiments Nos. 67–119, was similar except that the ice-bath and five-liter Pyrex bulb which it contained were replaced by the ice-bath and one-liter Jena glass bulb shown in Fig. 2. In making a determination the ice-bath, provided with a stirrer, was filled with chipped ice and distilled water. Following that the evacuated bulb was filled with ammonia from the storage bulb, C, to very nearly the desired pressure, i. e., one, two-thirds or one-third of an atmosphere, allowance being made for the corrections to be applied. Upon closing stopcock No. 16 the line was pumped down to that point. It developed that this operation required much more time than was at first anticipated. After allowing for temperature equilibrium to be established, ordinarily about three hours, the initial pressure was read. The ammonia was then condensed into bulb G with liquid air to varying final pressures, 0.0 to 40 mm. A total of twelve to fifteen hours was allowed for the condensation in the case of a zero residual pressure. Stopcock No. 16 was always closed during the final pressure readings. The

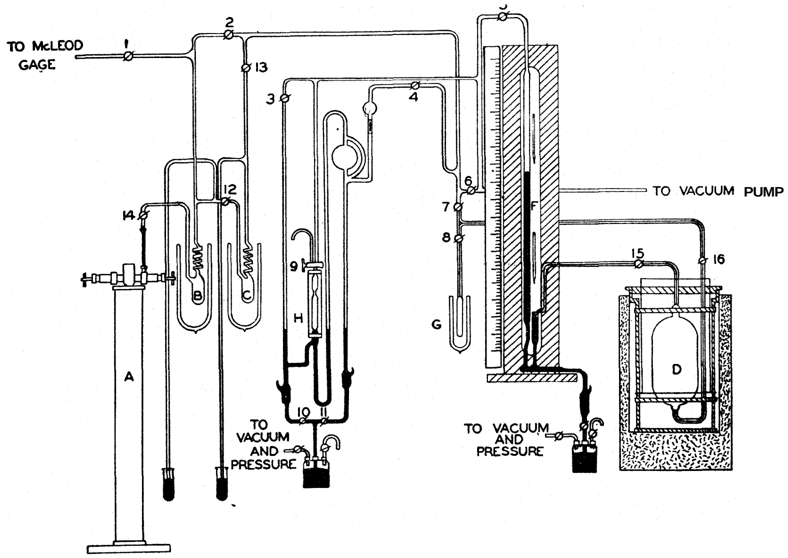

Fig. 1.—General arrangement of apparatus for gas density determinations.

last step consisted in sealing off the capillary extension of the bulb G while the latter was still immersed in liquid air. Necessarily before doing this the ammonia in the line down to stopcock No. 16 (5 l. bulb) and No. 17 (1 l. bulb) was condensed. During the early stages of the work a Toepler pump was used in testing for uncondensed ammonia after sealing off the bulb. This was subsequently found to be unnecessary. The details of weighing the bulbs, closed and open, will be discussed in a later section.

Purification of Ammonia

Synthetic anhydrous ammonia was used throughout the work, that for experiments Nos. 37–119 having been kindly donated by the Barrett Company through the courtesy of Doctor J. M. Braham. The steel cylinder, A, containing freshly cut sodium, was partially filled with the liquid and allowed to stand for several days. The system having been previously evacuated, ammonia was condensed in B by means of liquid air and subjected to several fractionations, the end portions being always discarded. Furthermore, at the end of each distillation the solidified ammonia was pumped until the pressure became less than 0.001 mm. The portion remaining was stored in C, the bulb being kept immersed in liquid air.

As far as could be observed there was no occasion to question this method of purification. Water and non-condensing gases should, on the basis of McKelvey and Taylor's[7] work, be the principal impurities and the treatment described above ought to eliminate completely these or any other foreign substances likely to be present. That such was the case seems evident from the following considerations. It was noted on the one hand in making as many as fifteen successive density determinations from a given portion in the storage bulb, with practically all of the ammonia being used, that no differences in the results could be detected. This obviously would indicate that the material was uniform, *i. e.*, there were no lighter and heavier fractions. Also, it was found that there was no indication of a permanent pressure developing in the bulb used for measuring the volume of the gas, in spite of the fact that the bulb was not pumped between successive determinations in a

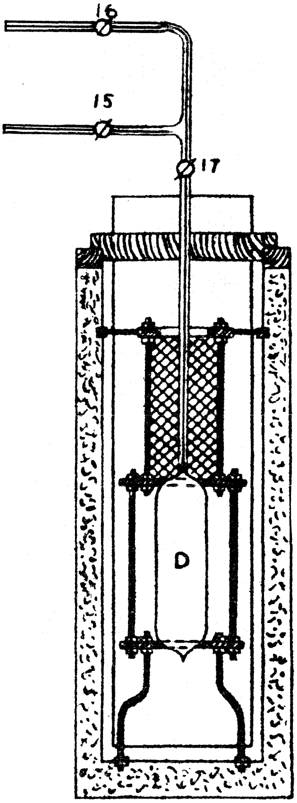

Fig. 2.—One-liter bulb and ice-bath.

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(7) McKelvey and Taylor, B.S., Sci. Paper No. 465, 1923.

given series. Non-condensing gases, especially hydrogen, must therefore have been absent.

Details of Procedure

(a) Volume.—As explained in the preceding section, two different bulbs were used for the volume measurements. The calibration of the five-liter Pyrex bulb was carried out by first filling it, at the ice-point temperature, with recently boiled, distilled water to fixed marks on the connecting capillaries. The water was weighed by draining it off into glass-stoppered flasks, the usual air buoyancy and calibration corrections being applied. That adhering to the walls was subsequently pumped out and collected in a liquid air trap that could be disconnected and weighed. Four independent determinations of the bulb volume were made before use and a second series of three a year and a half later. The deviation in all of these determinations was not greater than one part in **50,000.** The "stretch" of the bulb was determined and found to be **0.480** ml. per atmosphere. After connecting the calibrated bulb to the manometer and loading apparatus the volume of the exposed parts was **2.27** ml. Allowance was made for the temperature difference of the latter in estimating the effective volume of the bulb when filled with ammonia. The total volume included that of the bulb and the capillaries, through the bore of stopcock No. **16** (Fig. **1)** and to a fixed mercury level in the short arm of the manometer

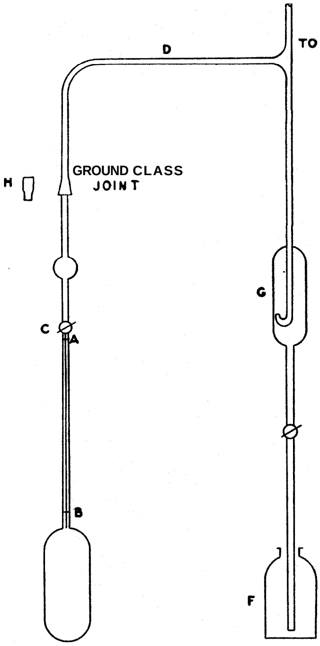
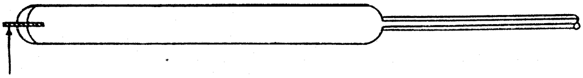


Fig. 3a.—One-liter bulb as set up for calibration.

The one-liter bulb was annealed in a tube furnace at 300° before being calibrated. It was then set up as shown, exclusive of the ice-bath, in Fig. **3a.** Before introducing water the bulb was evacuated and weighed with the ground-glass cap, H. Special precautions were taken to exclude air while the bulb was being filled with water. The reservoir above the stopcock served to allow for expansion upon removal from the ice-bath. Before being weighed the bulb and its contents were brought to room temperature. The net volume of the bulb and connecting capillary, including the bore of the stopcock plug, as obtained in five determinations was **1030.56** (±0.01) ml The "dead space" was in this case only **0.3** ml. with a correspondingly smaller correction for the exposed portion. The "stretch" of the bulb was found to be **0.087** ml. per atmosphere.



Platinum tube
Outside diameter **1.00** mm., wall thickness **0.05** mm.

Fig. 3b. —Condensing bulb.

(b) Temperature.—No direct measurements of the ice-bath temperatures were made. However, baths made up in a similar manner, with chipped ice and distilled water, have been tested very thoroughly in this Laboratory by J. M. **Gaines,** Jr., by means of platinum resistance thermometers and found to be constant within **0.003"** ***or*** **0.000** (±0.003) °C.

(c) Pressure.—The same manometer was used throughout all of the work. A great deal of time was devoted to improving the conditions under which the readings were made, especially as regards temperature control and illumination. In the following paragraph there is given a description of the manometer in its final form.

The glass tube of the mercury manometer, F (Fig. 1), had an internal diameter of 17 mm. and was placed in a heavy cast bronze case provided with a plate glass front and a frosted glass back. The sides were covered with felt. The bronze case was placed on a large slate slab, and a cabinet, the interior of which was painted black, built around it. The door on the front of the cabinet was provided with slots through which the observations could be made. Two different cathetometers, both of them Geneva instruments, were available for measuring the pressures. The first of these which was used in experiments Nos. 1–26 carried a silver scale on the column. The second cathetometer was one that had been made with a special device for clamping the telescopes rigidly in position and proved to be a very satisfactory instrument. This cathetometer did not have an attached metal scale, the readings being made on a glass standard meter bar that was set up at the left of the brass case. The scale on the meter bar was ruled in millimeters with a diamond chip by the Société Gknevoise d'Instruments de Physique. It was calibrated at Berne, Switzerland.

In Fig. 4 is shown the construction of the short arm of the manometer as suggested by F. G. Keyes. The fine glass tip served as a fixed mark to which the mercury level was brought while making readings. The mercury surface was illuminated with diffused light coming through the frosted plate glass and a slit in a semicircular brass plate surrounding the rear half of the glass tube. The electric light bulb could be moved up and down by means of an overhead pulley. It was found possible in this way to illuminate the mercury surface so as to get a sharply defined meniscus. The long arm of the manometer was provided with a movable brass plate and a lighting arrangement similar to the one just described. In the case of the glass scale the best results were obtained by illumination from the rear. The lights for this purpose were supported from the same bars that carried the bulbs for the mercury columns. After having made the necessary initial adjustments it was therefore possible to swing the cathetometer telescope directly from the mercury meniscus at any level to the illuminated glass scale. In doing this the spirit levels on the telescopes were always checked.

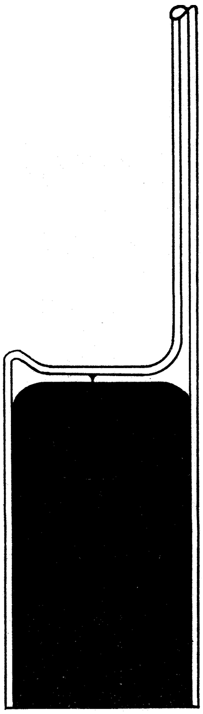


Fig. 4.—Short arm of manometer.

The temperature within the brass case was determined by means of two calibrated thermometers that could be read to **0.01°**. Ordinarily the temperature variations were considerably less than 0.1° during a given set of readings.

The vernier box of each telescope carried a circular head with a scale divided into one hundred divisions that could be estimated to tenths. When the cathetometer was at a distance of twenty-four inches from the manometer and the glass scale one millimeter on the latter corresponded to about a hundred and forty divisions. The following procedure was adopted in making observations. Five settings on the meniscus were first made in succession and the mean of these calculated. The telescopes were then swung over to the glass scale and two settings made on each of the millimeter divisions within which the meniscus level fell. By interpolation the fractional part of a millimeter was computed to the third place. Ordinarily eighteen sets of these observations were made on each mercury column, corresponding therefore to as many independent

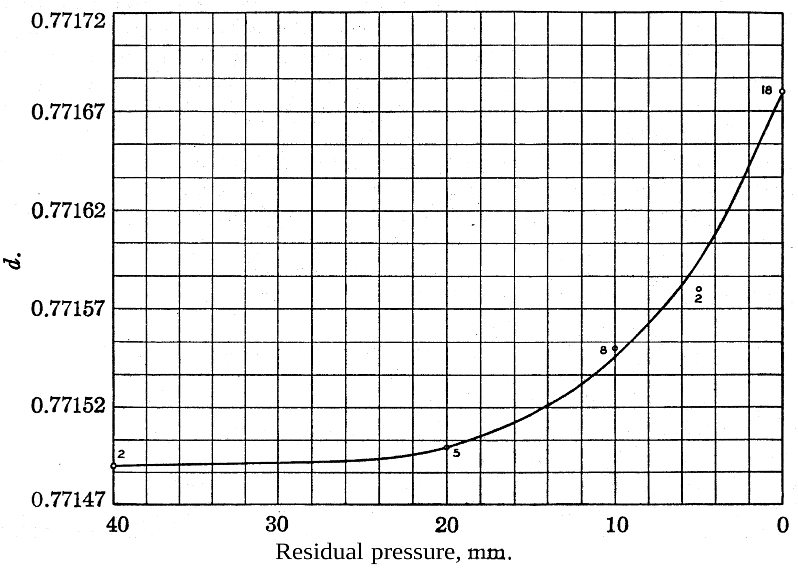


Fig. 5.

pressure determinations. The thermometers were read at the beginning and end of each set of three observations and a correction applied to the mean of these. As a precaution to guard against any lag the mercury columns were lowered at these same intervals and new settings made. By way of illustrating the degree of reproducibility the resultant six mean values for the last experiment, No. **119,** as obtained in pairs by three observers, are tabulated, temperature corrections having been applied.

	760.243
	760.231
	760.253
	760.255
	760.257
	760.246
Av.	**760.248**
Meniscus corr.	**$0.006**
Level corr.	**$0.030**
Gravity corr.	**−0.207**
Final corr. press.	760.077 (±0.01)

A correction for the difference in **curvature** of the two mercury surfaces was made by using the equation developed by Lohnstein.[8]

Since the short arm of the manometer and the one-liter bulb were not at the same level, there was a positive correction at one **atmosphere of 0.03 mm.**

The gravity correction was made by taking g_s = **980.665** cm./sec.^{2} and g_1 = **980.398** cm./sec.^{2}, the constant of gravity in Room **4-458** at M. I. T. The value **980.665 cm./sec.^{2}** is that adopted by the "International Critical Tables" and by Blanchard and Pickering in their review of the literature relating to gas densities.

(d) Mass.—As in the case of the pressures, much time was devoted to developing

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[8] Lohnstein, *Ann. Physik*, **33**, 296 (1910).

the technique of obtaining the weight of the ammonia. For that reason the procedure will be discussed in some detail.

(1) Condensing Bulbs.—Necessarily an important step in connection with the weighing was that of devising a form of bulb that could be opened without any loss of glass. In experiments Nos. **1–79,100, 102, 104, 106, 108** and **110** the Pyrex bulb was of the simple form illustrated in Fig. 1. This type was opened by first freezing the ammonia with liquid air in the capillary end. Upon removal from the liquid air a cloth was wrapped around the cooled portion and a fine flame applied at the other end. In view of the high vacuum existing the glass caved in upon melting and in doing so the particles of blown glass were carried along into the bulb. Following this the capillary end was again immersed in liquid air and the ammonia allowed to evaporate as the liquid air gradually disappeared. There was a tendency for the bulbs to crack unless they were handled in this manner. Before weighing the empty bulb it was put in a tube that could be evacuated in order to replace the remaining ammonia vapors with air.

The above type of bulb proved in the end not to be entirely satisfactory. In some unexplained way they did apparently undergo slight changes in mass while being opened They were accordingly abandoned in favor of a modification proposed by F. G. Keyes and illustrated in Fig. 3b. It had previously been found by Keyes and Kraus that platinum tubes of a high degree of purity and sufficiently thin walled could be sealed directly into Pyrex glass in such a way as to hold a vacuum at liquid air temperatures on the one hand and also to stand the vapor pressure of liquid ammonia at room temperature, approximately ten atmospheres. The outer end of the platinum tube was closed by welding with a fine flame The bulbs were opened by puncturing the platinum tube with a small needle. Density data obtained with these bulbs showed, when other disturbing factors had been eliminated, a high degree of consistency.

(2) Balances and Methods of Weighing.—Considerable difficulty was experienced in determining the weight of the bulbs with the degree of accuracy desired, *i.* e., 0.01 mg.[9] However, with the right kind of a balance and with due regard to the necessary air buoyancy correction involved this was definitely accomplished.

Four different balances were used, the last being a special fifty gram load, semi-micro balance with a sensitivity (displacement of the rest-point) of approximately thirteen scale divisions. The notched beam was divided into a hundred divisions and carried a one milligram rider. Both the substitution and the transposition methods were used in making the weighings. The latter seemed on the whole to give more consistent results. The weights, Class M, had been calibrated by the Bureau of Standards. A counterpoise in the form of an open bulb was always placed on the scale pan with the weights. The size of this was such that its mass would be a little less than that of the empty bulb being weighed. The scale pans were fitted with aluminum wire supports by means of which the bulbs could be kept in a vertical position. This was necessary especially in weighing the sealed bulbs with their liquid contents. The rest points were determined by taking three readings to the right and two to the left. In all cases the weight to the nearest milligram was obtained by placing the proper fractional weights on the pan. With the first three balances the fractional part of a milligram was in turn computed from the rest-point, no rider being required. In the case of the special semi-micro balance referred to above the rider was used for the tenths and the rest-points for hundredths of a milligram. No-load rest-points were obviously not needed in either the substitution or the transposition method.

The procedure adopted consisted in making a total of sixteen weighings, usually only four on any one day. In doing this the temperature within the balance case, the barometric pressure and the humidity were recorded at regular intervals. An elaborate

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(9) The authors are indebted to Mr. A. T. Pienkowsky of the Bureau of Standards for valuable suggestions in connection with the weighing.

set of tables was made up to simplify the work involved in obtaining the air densities. Since 1 cc. of air under ordinary conditions weighs approximately 1.2 mg. it was necessary to know the net volume displaced to within 0.01 cc. in making the air buoyancy correction. The volumes of the sealed bulbs were determined by means of hydrostatic weighings, whereas those of the open bulbs and the weights were calculated from the known densities of Pyrex glass, platinum, bronze and aluminum.

The following tabulation serves as an illustration of the degree of reproducibility obtained in making a series of weighings. The values given represent the mean, experiment No. 119, of each set of four weighings, after having been reduced to vacuum.

	Closed bulb	Open bulb
	2.243679	1.448758
	2.243673	1.448751
	2.243674	1.448747
	2.243677	1.448736
Av.	2.243676	1.448748
Calibration corr.	+0.000054	+0.000069
Final corr. wt.	2.243730 (±0.00001)	1.448817 (±0.00001)

(3) Residual Gas.—The equation of state used in calculating the weight of the residual ammonia, in those experiments where the final pressure was not zero, was obtained by assuming first the general equation

$$pv = RT_0 + (RT_0\alpha)p + (RT_0\beta)p^2$$

This was in turn put in the form

$$(pv)_1 = A + Bp_1 + Cp_1^2$$
$$(pv)_2 = A + Bp_2 + Cp_2^2$$
$$(pv)_3 = A + Bp_3 + Cp_3^2$$

In evaluating the constants the following approximate values were taken for the density of ammonia

1 atm.	0.77160 g./l.
$^2/_3$ atm.	0.51189 g./l.
$^1/_3$ atm.	0.25470 g./l.

By means of these densities the pv products per gram at the different pressures were calculated and a final equation of state for 0° obtained

$$pv = 1316.19 - 21.675p + 1.485p^2$$

p being expressed in atmospheres and v in cc. For the purpose of calculation the equation was put in the form

$$\text{wt. of residual ammonia} = \frac{\text{vol. of bulb}}{(1316.19/p) + 1.485p - 21.675}$$

Experimental Data and Discussion of Results

Altogether 119 density determinations were made, 88 at one atmosphere and 23 at lower pressures. The remaining eight were lost.

In Table I are presented the results with the five-liter Pyrex bulb at one atmosphere. It is to be noted that the density decreased from an average of 0.77168 at the lowest residual pressure to an average of 0.77149 at the highest. As will readily be seen from the accompanying curve, the latter seemed to represent a definitely limiting value. By way of confirmation it was decided to make a number of determinations with a bulb that had been baked and evacuated in order to remove the last traces of adsorbed water. It was thought that this would result in the complete elimination of any adsorption effects with ammonia and thus constant density data should be obtained regardless of the residual pressure. This proved in the end to be the case. However, before obtaining consistent results it became necessary to devise a new type of condensation bulb and also to observe additional precautions in avoiding adsorption effects in the line.

TABLE I

DENSITIES DETERMINED WITH 5-LITER PYREX BULB

Expt.	Approx. res. press., mm.	Density g./l.	Average	Expt.	Approx. res. press., mm.	Density g./l.	Average
4	0.0	0.77167		11	5.0	0.77163	
5	.0	154		21	5.0	153	0.77158
6	.0	169		1	10.0	141	
8	.0	176		7	10.0	166	
9	.0	177		27	10.0	162	
12	.0	174		36	10.0	157	
22	.0	161		40	10.0	143	
28	.0	190		43	10.0	163	
29	.0	134		55	10.0	153	
37	0	185		56	10.0	157	.77155
39	.0	177		42	20.0	146	
41	.0	175		52	20.0	145	
44	.0	169		53	20.0	152	
45	.0	153		61	20.0	153	
46	.0	158		62	20.0	156	.77150
47	.0	164		50	40.0	153	
48	.0	164		51	40.0	144	.77149
49	.0	168	0.77168				

In Table II will be found a summary of the results with the one-liter bulb. Experiments 67–79 were made with the first form of condensation bulb. The mean density values for the different residual pressures agreed very well. Nevertheless, the differences between individual determinations were greater than the accuracy of the measurements involved would lead one to expect. This led to some questioning of the method of opening the bulbs and it was accordingly decided to try the kind illustrated in Fig. 3b. The first two experiments, Nos. 80–81, agreed remarkably well. However, the next series, Nos. 82–92, was far less satisfactory. In the first place the densities were higher and furthermore they varied considerably. Five additional experiments, Nos. 94–98, all at zero residual pressure, were likewise such as to leave one in doubt.

TABLE II

DENSITIES DETERMINED WITH ONE-LITER JENA GLASS BULB (BAKED)

Expt.	Approx. res. press., mm.	Density, g./l.	Average	Expt.	Approx. res. press., mm.	Density g./l.	Average
67[a]	0.0	0.771305		94[a]	0.0	0.771584	
68	.0	1301		95	.0	1454	
69	.0	1387		96	.0	1469	
70	.0	1349	0.771281	97	.0	1450	
71	10.0	1425		98	.0	1435	0.771478
78	10.0	1227					
79	10.0	1336	.771269	99	.0	1457	
72	20.0	1336		101	.0	1332	
74	20.0	1234		103	.0	1366	
75	20.0	1200	.771197	105	.0	1337	
73	40.0	1320		107	.0	1357	
76	40.0	1378		109	.0	1377	.771371
77	40.0	1243	.771254	100	.0	1484	
				102	.0	1091	
80[b]	0.0	1307		104	.0	.769988	
81	.0	1308	.771248	106	.0	.771404	
				108	.0	1298	
89	.0	1448		110	.0	1508	.771129
90	.0	1476	.771402				
82	10.0	1379		111	.0	1311	
85	10.0	1425		112	.0	1332	
88	10.0	1478		113	.0	1236	
93	10.0	1407	.771362	114	.0	1305	
83	20.0	1515		115	.0	1293	.771297
86	20.0	1693					
91	20.0	1402	,771477	116	.0	1262	
84	40.0	1359		117	.0	1273	
87	40.0	1466					
92	40.0	1372	.771339	118	.0	1239	
				119	.0	1262	.771259

[a] **Indicates stages at which the bulb was baked.** [b] **The remaining experiments with the exception of Nos.** 100, 102, 104, 106, 108 **and** 110 **were made with the type of condensation bulb shown in Fig.** 3b.

In view of the above discrepancies it seemed advisable to obtain some comparative data with the two types of condensation bulbs. In the next series, therefore, Nos. 99–110, they were alternated. As in the case of the other series, the same sample of ammonia was used throughout. After having made the first experiment, No. 99, there were reasons for believing that the variable results might be due to slight traces of adsorbed ammonia in the line that had not been removed by evacuating before the condensation process was started. Up to this point the pumping had been continued for comparatively short periods, ordinarily about an hour, or at least until a McLeod gage gave no indication of any pressure. Beginning with No. 100 the line was pumped somewhat longer with consequent lower densities and also a much higher degree of consistency, *i. e.*, with the new style of bulb. The six determinations, Nos. 100, 102, 104, 106, 108 and 110, made with the first type showed conclusively that the weight of the glass could not have remained constant.

In the next five experiments the line was pumped even longer than in the preceding series, six to eight hours. The results showed a still further decrease in density. In order to determine if the limit of the adsorption effect had been reached, two additional experiments, Nos. 116–117, were made in which dry air was admitted from time to time while the line was being evacuated over a period of fifteen hours. Also, as a further check, in the next two experiments Nos. 118–119, the ammonia was removed by condensing it with liquid air in a second bulb that could be shut off with a stopcock during the subsequent condensation from the one-liter bulb. Since the maximum deviation of the four determinations was slightly less than four parts in seventy-five thousand, it was concluded that the adsorption effect had finally been eliminated and the average of these was accepted as the density of ammonia at 0°.

The authors realize that in selecting the last four values for determining the final mean density of ammonia no weight is given to the previous determinations. The gradual development of the method with consequent elimination of disturbing factors would seem, however, fully to justify this procedure.

Acknowledgment.—The authors wish to express their appreciation to Professor F. G. Keyes at whose suggestion this research was undertaken. His continued interest and helpfulness contributed much to the progress of the work. They are also greatly indebted to C. W. Orleman, Charles Rubin and Stanley L. Witcher, who assisted in the work with the one-liter bulb, especially in developing the technique of weighing.

Summary

A precision method for the determination of gas densities has been developed. An important feature of it is that it makes possible the definite elimination of adsorption effects. Also, the method readily lends itself to use over a wide range of temperatures.

On the basis of the data presented, the normal density of ammonia is considered to be 0.77126 (±0.00001)

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The Density of Ammonia at Reduced Pressures and its Relation to the Atomic Weight of Nitrogen, the Gas Constant, R, and the Limiting Molal Volume, V_0

BY GERHARD DIETRICHSON, C. W. ORLEMAN AND CHARLES RUBIN

Introduction

Density determinations at reduced pressures are of particular importance because of the various computations that are thus made possible. The only previous work recorded, in the case of ammonia, is that by Moles and Batuecas.[1] Using the same method employed in determining the normal density,[2] they obtained the values

$^2/_3$ atm..	**0.511815** g./l.
$^1/_2$ atm..	**,382925** g./l.
$^1/_3$ atm.	.254607 g./l.

On the basis of these densities, combined with the previously determined normal density of 0.77169, they found the molecular weight of ammonia to be 17.032 and the atomic weight of nitrogen to be 14.009.

Procedure

The present work was carried out along precisely the same lines as that by Dietrichson, Bircher and O'Brien[3] in determining the normal density of ammonia. A number of preliminary experiments had been made by them at each of the pressures, two-thirds and one-third of one atmosphere, using the five-liter Pyrex bulb for measuring the volume of the gas. The latest results have all been obtained with the one-liter Jena glass bulb. In connection with these determinations it is desired to emphasize once more the precautions observed in eliminating the adsorbed ammonia in the line. This was accomplished in two ways. In some cases it was removed by evacuating over a period of fifteen hours, the pumping being interrupted from time to time and dry air admitted. Figure 1 shows the arrangement that was used in other instances. In these cases the adsorbed ammonia was first condensed in bulb **A.** Stopcock No. 1 was then closed during the subsequent condensation from the one-liter bulb. The condensing bulbs were similar to those used in the previous work. Also, the ammonia was subjected to the same purification process. Allowance was made in all of these experiments for the change in volume of the five-liter and the one-liter bulbs with pressure.

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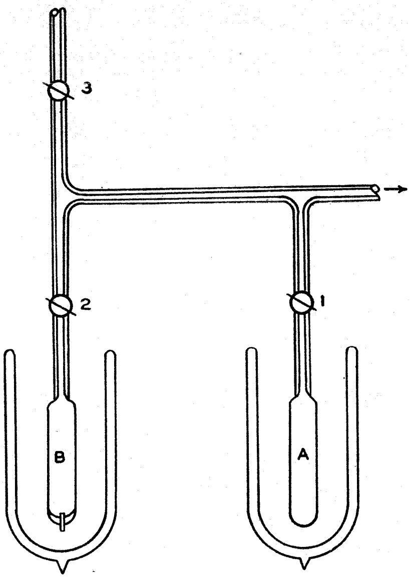
(1) Moles and Batuecas, *Anales Soc. Españ. fís. quím.*, **28, 871 (1930).**

(2) Moles and Batuecas, *Sitz. Akad. Wiss. Wien, 138,* **779 (1929).**

(3) Dietrichson, Bircher and O'Brien, THIS JOURNAL, **55, 1 (1933).**

Experimental Data

Nine determinations were made at two-thirds of an atmosphere using the five-liter bulb and six with the one-liter bulb. Table I contains these results. The corresponding numbers at one-third of an atmosphere, as shown in Table II, were fourteen and four.



To one-liter **bulb** and short arm of manometer.

Fig. 1.—A, condensing **bulb** for ammonia in line; B, condensing **bulb** for ammonia in 1-liter **bulb.**

TABLE I

DENSITY OF AMMONIA AT $^{2}/_{3}$ ATM.

As determined with 6-liter Pyrex bulb				As determined with 1-liter Jena glass bulb (baked)			
Expt	Approx res. press., mm.	Density, g./l.	Average	Expt.	Approx. res. press., mm.	Density, g./l.	Average
16	0.0	0.51190		120	0.0	0.511590	
24	.0	.51191		121	.0	.511631	
32	.0	.51201	0.51194				
13	5.0	.51199		122	.0	.511609	
14	5.0	.51172		123	.0	.511613	
28	5.0	.51185	.51186				
15	10.0	.51179		124	40.0	.511586	
30	10.0	.51189	.51184	125	40.0	.511599	0.511605
31	15.0	.51166	.51166				

The results obtained with the five-liter Pyrex bulb at the lower pressures varied as did those at one atmosphere, *i. e.*, the densities decreased with increasing residual pressures. However, the limiting values were still higher than the densities as later determined with the one-liter bulb which

TABLE II

DENSITY OF AMMONIA AT $^1/_3$ ATM.

As determined with 5-liter Pyrex bulb

Expt.	Approx. res. press., mm	Density, l	Average
18	0.0	0.25492	
20	.0	.25471	
57	.0	.25487	
58	.0	.25482	
59	.0	.25474	0.25482
17	5.0	.25480	
26	5.0	.25467	
35	5.0	.25473	.25473
19	10.0	.25478	
34	10.0	.25466	
63	10.0	.25470	
64	10.0	.25467	.25470
65	20.0	.25471	
66	20.0	.25470	.25471

As determined with 1-liter Jena glass bulb (baked)

Expt.	Approx. res. press., mm.	Density, g./l.	Average
126	0.0	0.254559	
127	.0	.254575	
128	.0	.254598	
129	.0	.254576	0.254576

had been baked before being used. Experiments Nos. 120–125 are divided into three groups of two each. In Nos. 120–121 the adsorbed ammonia in the line was pumped out under conditions as previously described. In Nos. 122–123 it was condensed in bulb A. Finally in Nos. 124–125 the residual pressure instead of being zero was about 40.0 mm., the absorbed ammonia in the line being removed by pumping. It is significant that the six density values obtained under these varying conditions agree to within slightly less than five parts in fifty thousand. The close agreement between the first four and the last two determinations also seemed to prove conclusively that the absorption effect in the one-liter bulb, as well as in the line, had been eliminated completely. The density at two-thirds of an atmosphere was accordingly considered to be 0.51161 (±0.00001).

Four density determinations at one-third of an atmosphere, Nos. 126–129, corresponding to Nos. 120–123 at two-thirds, resulted in a mean value of 0.25458 (±0.00001).

Discussion of Results

In the paper by Dietrichson, Bircher and O'Brien it was pointed out that the density of ammonia could be calculated by means of an equation of the form

$$d_n = \frac{m}{v_1} = \frac{M(1 + \bar{\lambda})}{RT_0}$$

Correspondingly, by using experimentally determined densities, it is possible to compute molecular weights and from these in turn atomic weights. Obviously in doing this it is necessary to assign values to R, T_0 and λ. Molecular and atomic weights obtained in this manner will therefore be significant only in so far as these constants, or quantities equivalent to them, are accurately known.

The limitations involved in the above method of determining atomic weights, which was originally proposed by Guye, have been admirably set forth in a paper by Baxter[4] entitled "The Significance of the Density of Hydrogen Bromide with Reference to the Atomic Weight of Bromine." Attention is called especially to the uncertainty with regard to λ which he defines by the equation $p_0v_0/p_1v_1 = 1 + \lambda$, *i. e.*, the ratio of the pressure–volume product at zero pressure to that at one atmosphere, and computed from density data at different pressures. As Baxter states, however, various procedures have been adopted in extrapolating for the p_0v_0 products with consequent variations in λ. The two that are discussed are referred to as a "method of secondary differences" and an "algebraic method." In effect these are the same mathematically in that both assume a quadratic rather than a linear relation.

In his own subsequent determinations of the density of oxygen, nitrogen and the rare gases, Baxter[5] obtains the pv/p_1v_1 ratios at two or three pressures below one atmosphere and then, by using the method of first differences, extrapolates each of these to zero pressure for $p_0v_0/p_1v_1 = 1 + \lambda'$.[6] Moles in his papers on ammonia follows essentially the same procedure except that he finds d/p, or $1/pv$, for each pressure and applies the method of first differences to these values in order to get a limiting density, d_0/p_0 or $1/p_0v_0$. Using his notation, the equation is written in the form, $L_0/L_{\text{Lim.}} = 1 + \lambda''$, which corresponds to

$$\frac{1/p_1v_1}{1/p_0v_0} = \frac{d_1/p_1}{d_0/p_0} = \frac{L_0}{L_{\text{Lim.}}} = 1 + \lambda''$$

In this equation p_1, v_1 and d_1 represent the values of these quantities at one atmosphere and p_0, v_0 and d_0 the limiting values at zero pressure. Moles, as does Baxter, calculates a separate λ to correspond to each pressure at which density determinations have been made and takes the mean as his final value, As will be illustrated in Table III, treatment of the same set of density data by these two operations does not give identical results. That is what one would expect if the pressure–volume product, pv or d/p, is a quadratic rather than a linear function of the pressure.

The situation with regard to the method of differences as applied to determining the value of λ can possibly best be illustrated by means of curves, Fig. 2, showing the variations of pv and of d/p with p for ammonia. If plotted on a sufficiently large scale it is found that, in general, there is a curvature. It necessarily follows that extrapolation to zero pressure

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(4) Baxter, THIS JOURNAL, 44, 595 (1922).

(5) Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, 10, 479 (1924); 11, 231 (1925); 12, 20 (1926); 12, 699 (1926); 14, 50 (1928); 15, 441 (1929).

(6) For the sake of differentiation, the λ as defined by Baxter will be designated as λ', that by Moles as λ'' and that by the authors of this paper as λ'''.

TABLE III

ATOMIC WEIGHTS FROM GAS DENSITIES

Density	NH_3 D. B. O. and D. O. R.	NH_3 M. and B.
g./l. 1 atm.	0.77126	0.77169
$^2/_3$ atm.	.51161	.51181
$^1/_2$ atm.		.38293
$^1/_3$ atm.	.25458	.25461
$pv = a + bp + cp^2$	$pv = 1315.403 - 17.767p - 1.054p^2$	$pv = 1316.025 - 20.4529 + 0.192p^2$
$p_0v_0/p_1v_1 = 1 + \lambda'$	1.014901	1.01540
$M = v_0d_n/(1 + A')$	17.0335	17.0346
At. wt. N	14.0101	14.0112
$L_0/L_{\text{Lim.}} = 1 + \lambda''$	1.015003	1.01552
$M = v_0d_n/1 + A''$	17.0318	17.0323
At. wt. N	14.0084	14.0089
$(1/pv)_{p\rightarrow 0}\,[\partial(pv)/\partial p]_T = \lambda'''$	0.015109	0.015249
$M = v_0d_n/(1 + \lambda''')$	17.0300	17.0372
At. wt. N	14.0066	14.0138

becomes increasingly uncertain the greater this effect. In the case of ammonia the curvature is quite pronounced, especially with the data as reported in this paper.

The authors feel that the coefficient of deviation from Boyle's law should be defined as $\left(\frac{1}{pv}\right)_{p\rightarrow 0}\left[\frac{\partial(pv)}{\partial p}\right]_T = A'''$. An evaluation of λ when so defined naturally necessitates an equation of state in terms of p and v. Using the method of least squares, the densities being weighted in proportion to pressures, the following equation per gram of ammonia at 0° was developed.

$$pv = 1315.403 - 17.767p - 1.054p^2$$

For purposes of comparison a similar equation was developed for Moles and Batuecas' data on ammonia. Table III presents a summary of the various computations involved. The value for v_0 as obtained by Baxter and Starkweather in their work on oxygen was used throughout.

$$v_0 = RT_0 = \frac{M(1 + \lambda)}{d_n} = \frac{32 \times 1.00092}{1.42897} = 22.4144$$

It will be noted that the atomic weight of nitrogen, that of hydrogen being assumed to be 1.0078, was found to show considerable variation. It appears therefore that the gas density method for the determination of atomic weights cannot at present be considered as reliable as that based on gravimetric analyses, not because of insufficient accuracy as regards the gas densities, but rather because of uncertainties in connection with λ, R and T_0 (also $v_0 = RT_0$). This conclusion is in accordance with that stated by Baxter in his paper on hydrogen bromide.[4]

In view of the above considerations it seems therefore more profitable at present to use density data for the purpose of determining more accurately the value of R, the gas constant and v_0, the limiting mold volume at 0°. This can be done by considering that the constant, a, in the linear or quadratic equation is equivalent to RT_0/M. In other words, $pv = RT_0/M + bp$ or $pv = RT_0/M + bp + cp^2$. An evaluation of R and v_0 requires accordingly the constant, a, as obtained from the equation of

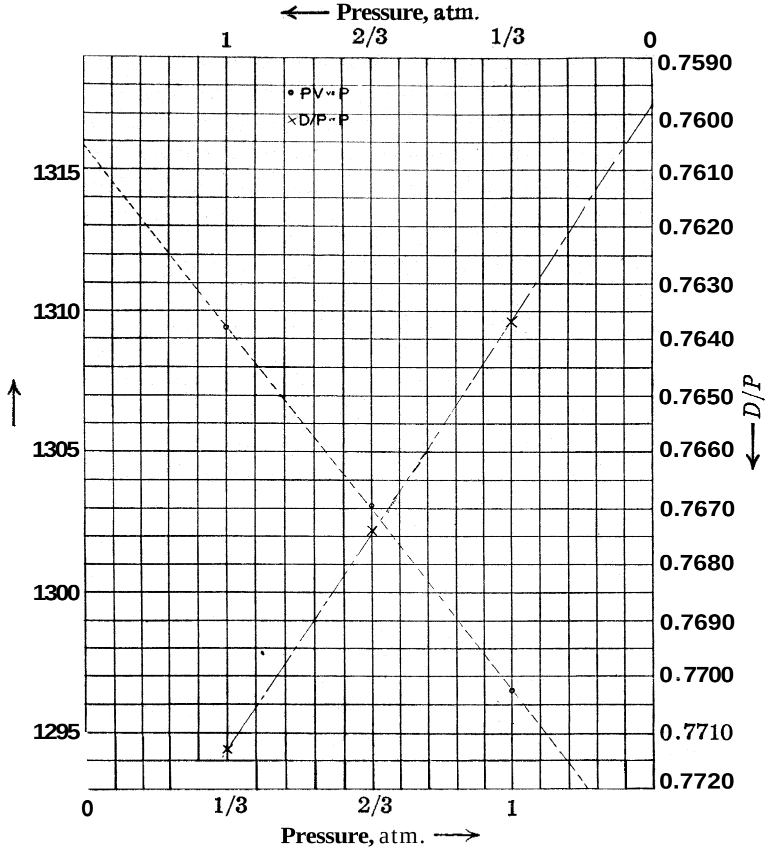

Fig. 2.

state and assumed values for T_0 and the atomic weights involved. Table IV presents a summary of the calculations that were made with the two forms of equation. The constants, a, b and c, were in each case determined as previously explained, *i. e.*, by using the method of least squares, the densities being weighted in proportion to the pressures. The following tabulation indicates the number of density determinations involved.

Pressures in atm.	1	$^2/_3$	$^1/_2$	$^1/_3$
NH_3 (D. B. and O. and D. O. and R.)	4	6		4
NH_3 (M. and B.)	39	17	18	23

A comparison of R and v_0 fails to show agreement in the case of either form of equation. In view of the known curvature of ammonia in plotting pv or d/p against p one would expect the best results with the second power equation. However, it must be kept in mind that a determination of these constants by the equation of state method involves again a more or less uncertain extrapolation. In other words, it is assumed that the curvature between zero and one-third of an atmosphere will be the same as that between one-third and one atmosphere. Density data at still lower pressures would obviously be helpful in settling this question. Also, additional data on other gases are needed. Among these carbon dioxide is of particular interest since the atomic weight of carbon has been determined with such accuracy and, furthermore, the proportion of carbon to oxygen is small. Density determinations of carbon dioxide by the method described in this and the preceding paper are now under way.

The value of R given in the "International Critical Tables," 82.06 cc. atm., is that derived by Keyes[7] on the basis of equations of state involving the densities of hydrogen, nitrogen, oxygen and carbon dioxide. The accuracy, however, is probably not greater than one part in two thousand. About the same time Henning[8] reported a value of 82.04 (±0.03).

In connection with the above, attention may be called to the fact that the second derivative of the equation derived from the authors' data is -2.108, the curvature therefore being convex upward in the range from zero to one atmosphere. This is in agreement with the compressibility isotherms at 25 and 50° as reported by Meyers and Jessup,[9] who obtained data extending into the low pressure region.

TABLE IV

THE GAS CONSTANT, *R*. AND THE LIMITING MOLAL VOLUME, v_0

$pv = a + bp \quad a = RT_0/M \quad T_0 = 273.16\,°\mathrm{K}.$

	a	b	M	R	$v_0 = RT_0$
NH_3 (D. B. and O. and D. O. and R.)	1316.484	-20.066	17.0312	82.081	22,421.3
NH_3 (M. and B.)	1315.940	-20.177	17.0312	82.047	22,412.0

$pv = a + bp + cp^2 \quad a = RT_0/M \quad T = 273.16\,°\mathrm{K}.$

	a	b	c	M	R	$v_0 = RT_0$
NH_3 (D. B. and O. and D. O. and R.)	1315.403	-17.767	-1.054	17.0312	82.015	22,403.2
NH_3 (M. and B.)	1316.025	-20.452	$+0.192$	17.0312	82.053	22,413.6

The equations for these are as follows

$$pv_{25°} = 1436.16 - 14.700p - 0.220p^2$$
$$pv_{50°} = 1552.86 - 10.314p - 0.193p^2$$

The densities obtained by Moles and Batuecas result in a curvature in the opposite direction.

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(7) F. G. Keyes, Am. *Soc. Refrig. Eng. J.*, 8, 505 (1922).

(8) F. Henning, Z. *Physik*, 6, 69 (1921).

(9) Meyers and Jessup, *Refrig. Eng.*, 11, 345 (1925).

Summary

1. The density of ammonia at two-thirds and one-third of an atmosphere has been determined and found to be 0.51161 (±0.00001) and 0.25458 (±0.00001).

2. The gas density method for the determination of atomic weights has been discussed.

3. The gas constant, R, and the limiting molal volume, v_0, have been computed by means of linear and quadratic equations of state developed on the basis of density data for ammonia as determined by the authors and by Moles and Batuecas.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. I. Conductance as Influenced by the Dielectric Constant of the Solvent Medium[1]

BY CHARLES A. KRAUS AND RAYMOND M. FUOSS[2]

I. Introduction

While solutions of electrolytes in solvents of high and of intermediate dielectric constant have been studied extensively, similar solutions in solvents of very low dielectric constant have not been investigated systematically. We know only that such solutions generally are poor conductors and that the equivalent conductance falls rapidly with decreasing concentration.

In addition to a number of isolated observations on the conductance of solutions in benzene,[3] and several series of measurements relating to the conductance of complex compounds in various solvents at relatively high concentrations,[4] the literature includes two important papers by Walden and his co-workers, who investigated[K] the conductance of a variety of *salts* in benzene, ether, carbon tetrachloride and similar solvents. According to Walden's measurements, the equivalent conductance of solu-

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(1) This paper comprises a part of the subject matter of a thesis submitted by Raymond M Fuoss in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) Jesse Metcalf Fellow in Chemistry in Brown University, **1931-1932**

(3) Kablukov, Z. *physik. Chem.*, **4, 430** (1889), hydrogen chloride in ether and in benzene; Cady and Lichtenwalter, THIS JOURNAL, **35, 1434 (1913)**; Cady and Baldwin, *ibid.*, **43, 646** (1921), heavy metal soaps in benzene; La Mer and Downes, *ibid* , **53, 888** (1931), conductimetric titrations in benzene: Hill, *ibid.*, **44, 1164** (1922), silver perchlorate in benzene

(4) Complexes in ether, Plotnikov, Z. *physik. Chem.*, **57, 502** (1906); Ussanowitsch, *ibid*, **124, 427 (1926)**: Bruns, *Z. anorg. allgem. Chem.*, **163, 120** (1927); complexes in bromine, Plotnikov, Z. *physik Chem.*, **116, 111 (1925)**; Finkelstein, *ibid.*, **121, 46** (1926); Plotnikov and Jakubson, *zbid* , **138, 235 (1928)**; Plotnikov and Kudra, *ibid* , **145, 625 (1929)**; complexes in toluene, xylene, and benzene, Plotnikov and Jakubson, *ibid.*, **147, 227 (1930)**; Jakubson, *ibid.*, **118, 31 (1925)**; Rabinowitch, *ibid*, **132, 83 (1928)**

(5) Walden, Bull. *Acad. Imp. Sci. St. Pel*, *7*, **934** (1913); Walden, Z *physik Chem.*, **147, 1 (1930)**

tions of quaternary ammonium salts in benzene falls off sharply with increasing concentration over the concentration range studied, namely, 0.1–0.03 N. In solvents of somewhat higher dielectric constant, the conductance passes through a minimum at moderate concentration and thereafter increases.

It is uncertain whether or not the equivalent conductance of electrolytes in benzene and similar solvents continues to fall indefinitely as the concentration decreases; the laws governing the conductance phenomenon in solvents of low dielectric constant are yet to be established. While the influence of the dielectric constant on conductance is satisfactorily accounted for by the interionic attraction theory in solvents of high dielectric constant, it is not known to what extent interionic forces are primarily concerned in solvents of low dielectric constant. Nor is it known to what extent a mass action effect may he involved. The present investigation was undertaken in order to obtain experimental information bearing on these auestions.

Benzene and dioxane $\left(\overline{\mathrm{CH_2CH_2OCH_2CH_2O}}\right)$ were chosen as solvents of very low dielectric constant. Solvents of any desired higher dielectric constant were obtained by adding solvents of high dielectric constant in proper proportion. For this purpose, water and ethylene dichloride were used. The conductance phenomenon has thus been studied in mixtures of dioxane and water over a dielectric constant range from **2.2** to 79 and in mixtures of ethylene dichloride with dioxane and with benzene over the range from 2.2 to **10.4.**

Tetraisoamylammonium nitrate and thiocyanate and tri-isoamylammonium picrate were employed as electrolytes; the first two are strong electrolytes, while the last is a relatively weak electrolyte. The conductances in the various pure and mixed solvents were determined over the (approximate) concentration range **0.00001–0.2** *N*, which was sufficient to establish the general characteristics of the conductance curves.

Because of the very low conductance of the more dilute solutions in solvents of low dielectric constant, the resistances were measured by means of a direct current galvanometric method. While the precision of this method is only approximately 1%, the results obtained with it are reliable within this limit as was shown by checking against results obtained by the usual alternating current method.

II. Materials

Tetraisoamylammonium Salts.—The iodide is best prepared as follows. An equivalent mixture of tri-isoamylamine and isoamyl iodide is introduced into a long tube which is then heated near the top to about 150°. As crystals of the salt form, they fall to the cooler region at the bottom, thus avoiding much of the decomposition which occurs if the salt is heated to higher temperature for an appreciable length of time. The product is washed with petroleum ether, and treated with potassium hydroxide in alcoholic solution to decompose any tertiary salt that may have formed during the heating. The salt is then precipitated by pouring the solution into water. After washing and drying, and rewashing with petroleum ether, a product is obtained which melts at 115°. This material, after several recrystallizations from a mixture of *anhydrous* ethyl acetate and petroleum ether, yielded a product melting at 136°

Anal. Subs., 0.3499, 0.4051, 0.4530: AgI, 0.1933, 0.2240, 0.2498 Calcd. for $(C_6H_{11})_4NI$: I, 29.85. Found: 29.87, 29.88, 29.81, av., 29.86.

Tetraisoamylammonium nitrate was prepared by treating the iodide with an exact equivalent of silver nitrate in alcoholic solution After filtering out the silver iodide, the solution was allowed to evaporate at room temperature, and the product was recrystallized from *a* mixture of anhydrous ethyl acetate and petroleum ether.

Tetraisoamylammonium thiocyanate was prepared by dissolving the nitrate in *absolute* alcohol and adding an exact equivalent of an analyzed solution of potassium thiocyanate in absolute alcohol. After filtering and evaporating the solution, the salt was recrystallized from anhydrous ethyl acetate and petroleum ether.

Anal. Subs., 0.8857, 0.5031: AgSCN, 0.4158, 0.2350. Calcd. for $(C_5H_{11})NSCN$: SCN, 16.29. Found: 16.42, 16.34.

In the first analysis, the silver nitrate was dissolved in water; in the second, the precipitation and first washing were carried out with alcohol. Since tetraisoamylammonium thiocyanate is only sparingly soluble in water, co-precipitation of the quaternary salt apparently occurred

It may be mentioned that the iodide is only sparingly soluble in water, the bromide may be recrystallized from water, while the chloride is extremely soluble and is very hygroscopic.

Tri-isoamylammonium picrate was prepared by adding a saturated hot alcoholic solution of picric acid to a slight excess of tri-isoamylamine. The crude product, which crystallizes from the alcohol almost completely on cooling, was recrystallized from ethylene dichloride and petroleum ether.

Dioxane was purified according to Vingee's method.[6] The technical product was cooked with caustic soda, dried over barium oxide, and subsequently distilled fractionally from sodium–lead alloy (NaPb). The middle fraction (about 90% of the total) was dissolved in liquid ammonia and treated with metallic sodium to remove various reducible impurities.[7] After boiling off the ammonia, the dioxane was redistilled and stored over sodium–lead alloy in a still from which it could be distilled directly into the conductance cells; m. p. 11.7°.

Benzene.—Thiophene-free benzene was washed with concentrated sulfuric acid, water, dilute potassium hydroxide solution and water. After drying, it was fractionally crystallized and stored in a still similar to the one used for dioxane; m. p. 5.43°.

Ethylene dichloride was distilled from phosphorus pentoxide. The middle fraction was stored over phosphorus pentoxide in one of the supply stills; b. p. 82.4° at 747 mm.

III. Apparatus and Method

Electrical Equipment.—Resistances up to 100,000 ohms were measured by the alternating current method. The apparatus was of the conventional type, comprising a drum wound bridge, a Vreeland oscillator, a set of Curtis resistance coils up to 100,000 ohms, condensers for balancing out capacity effects, a two-stage amplifier and telephones.

Higher resistances were measured by a direct current method, which essentially

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(6) Vingee, Thesis, Brown University, 1931.

(7) According to a later procedure of Vingee, the impurities are removed by boiling the dioxane with metallic sodium, after previous treatment with sodium hydroxide and desiccation with barium oxide This procedure is much more convenient than the treatment in ammonia.

amounted to using a galvanometer as ammeter, and computing the cell resistance by Ohm's law from the current so determined and the voltage applied to the conductance cells. Two galvanometers were used. The first (G_1) had a resistance of 15.6 ohms and a sensitivity of 3 X 10^{-8} amp./cm., the second (G_2) had a resistance of 913 ohms and a sensitivity of 4 X 10^{-10} amp./cm. The galvanometers were mounted on Julius suspensions, and covered with copper shields having windows opposite the mirrors. The sensitivity of the galvanometers was determined at frequent intervals during each experiment. By means of a suitable resistance in series and shunt with the galvanometers, any input current from 10^{-4} to 10^{-8} amperes could be adjusted to give full scale deflection (25 cm.).

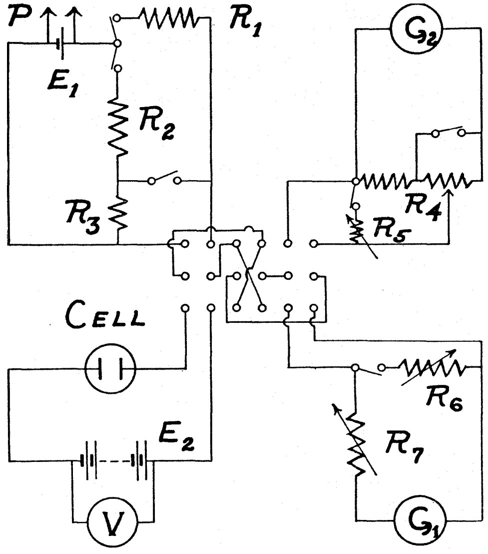

Fig. 1.—Direct current equipment: G_1, 15.6-ohm galvanometer; G_2, 913-ohm galvanometer; R_5, Re, R_7, 0–10,000-ohm variable resistances; R_4, 1–100,000-ohm Ayrton shunt; E_1, 1 5-volt dry cell; P, potentiometer leads; R_1, 1,000,000 ohms; R_2, 10,000 ohms; Ra, 1 ohm; E_2, 150-volt storage battery; V, Weston voltmeter.

The d. c. circuit is shown in Fig. 1. Two 0–10,000 ohm resistances R_6 and R_7 were used to control the sensitivity of galvanometer G_1. An Ayrton shunt R_4 (1–100,000 ohms) was used with the high sensitivity galvanometer G_2; an auxiliary shunt R_5 (0–10,000 ohms) and a shorting switch for half of the Ayrton coil gave intermediate steps between the ten-fold sensitivity changes obtained by R_4 alone. The calibrating circuit included a dry cell El, potentiometer (leads) P and resistances R_1 (1,000,000 ohms), R_2 (10,000 ohms) and R_3 (1 ohm) All resistances were calibrated to 0.1%.

The reversing switch permits the average of right and left swings to be taken and avoids zero point correction as well as permanent distortion of the galvanometer suspension due to repeated full deflection in one direction. The galvanometer deflections could be read to 0.3 mm., but were not reproducible to less than 1 mm. (out of the total deflection of 250 mm.), probably due to stray currents of various kinds in the control resistances. These were reduced to a minimum by keeping the total resistance of the galvanometer circuit as high as conveniently possible. One centimeter deflection on the 913-ohm galvanometer corresponded to a resistance of 4×10^{11} ohms, and a conductance of 5 X 10^{-14} mhos (for a cell with a constant equal to 0.02 and using 150 volts).

The source of current was a battery of 72 lead storage cells which were used when the e. m. f. was on the flat part of the discharge curve. The errors due to internal resistance of the battery and to polarization of the conductance cell (that is, in assuming that the voltage read on the Weston voltmeter V was the e. m. f. producing the current measured on the galvanometers) were determined and found to be less than one per cent., provided at least 150 volts were used. All lead wires were insulated by means of paraffined glass tubes, and the thermostat liquid in which the conductance cell was placed was a good grade of high flash petroleum oil. Practically no error was introduced by faulty insulation; the leakage corresponded to 1–3 mm. on the high sensitivity galvanometer in the most unfavorable cases, and was considered in the corrections.

The results of the alternating and direct current methods of measurement were compared directly for resistances of the order of 100,000 ohms. Lower resistances could not be measured with the d. c. method on account of the relatively high currents, while higher resistances could not be measured with the a. c. method without unbalancing the bridge. Indirect comparisons of the two methods were obtained, however, by measuring the ratio of the cell constants of several cells, first at low resistances (1000–10,000 ohms) by the a. c. method and second at high resistances (1–10 megohms) by the d. c. method. The a. c. and d. c. results agreed within 1% for both direct and indirect comparison.

Conductance Cells and Accessories.—The cells were constructed from Pyrex Erlenmeyer flasks by sealing side bulbs containing electrodes to the bottoms of the flasks. Long (20 X 0.8 cm.) necks with ground-glass stoppers were attached to the flasks in order to minimize the diffusion of moisture into the cells during introduction of solution. The necks were ground to fit the delivery tubes from the various solvent stills. The electrodes were lightly platinized; heavy platinization caused considerable adsorption in dilute solutions, while bright electrodes failed to give steady d. c. resistances. The cells were calibrated by comparing them against each other and against a specially constructed calibration cell whose constant was determined, using Parker's[8] data for 0.1 demal potassium chloride solution. The cell constants are given in Table I.

TABLE I

CELL CONSTANTS

Cell	Determined constant			Average
Calibration	21.626	21.635[a]		21.63
125 cc.	0.17790	0.17780	0.17769	0.1777
250 cc. (first)	.02544	.02552		.02548
250 cc. (second)	.015624	.015649		.01564
500 cc.	.19378	.19369	.19369	.1937

[a] Two separately prepared KCl solutions.

The purified solvents were stored in 3-liter Pyrex flasks, to which were sealed reflux columns and condensers. To the delivery tube of each condenser was sealed a 30-cc. bulb containing electrodes (cell constants 0.02 to 0.03). which permitted control of the specific conductance of the solvent as distilled and before admitting it to the conductance cell. Siphons from the test bulbs were provided with ground-glass joints which fitted the necks of the cells. The best figures for solvent conductance were as follows: dioxane, 5×10^{-15}; benzene, $< 3 \times 10^{-15}$; ethylene dichloride, 3×10^{-10} mhos. In each experiment, the solvent conductance was determined before adding solute and was subtracted from the observed conductance if the correction exceeded 0.5%. The cells were immersed in a thermostat kept at 25.00 ± 0.02°. When room temperature was under 25°, the necks of the cells were kept at about 35° by an electrically heated cap in order to prevent solvent from distilling into the necks. Precautions were taken to keep the glassware dry.

Method.—After making up solutions in different ways and comparing the results in order to locate and avoid any systematic errors in determining concentration, the following method was adopted. Solvent was distilled into one of the larger cells and a small portion of this was pumped by dry air pressure onto a weighed quantity of salt, in the small cell. The amount of solvent in each cell was determined by weighing. After diluting several times, the final solution (A) in the small cell was pumped into a weight buret, and increasing portions of this solution were weighed into the solvent in the first cell. For very dilute solutions, about one gram of solution (A) was weighed

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(8) Parker and Parker, THIS JOURNAL, 46, 332 (1924).

from a pycnometer into about 60 g. of solvent in a weight buret, and this was, in turn, weighed into the first cell in six to eight portions before starting to weigh in the remainder of solution (A).

Specific gravities were determined by means of a Westphal balance, and normalities were computed from the known weight concentrations.

IV. Results

The experimental results are summarized in Tables 11–XI, where c is concentration in equivalents of solute per liter of solution, and A is equivalent conductance. The values given in these tables were obtained by interpolation (and occasional extrapolation over a small distance) of the actual results on a large-scale log A–log c plot. The round concentrations chosen correspond to approximately equal steps on a log *c* scale, spaced at about the same ratio as the experimental dilution ratio. There are, of course, certain disadvantages in reporting only interpolated values, particularly when the interpolation function is arbitrary and not monotonic, but compact presentation of the large number (about fifty series of conductance measurements) of determinations could not otherwise have been achieved. For discussion and comparison, the conductance curves for the various systems investigated are shown in Figs. 2–5, where the open circles represent the *observed* values.

The conductance values for tetraisoamylammonium nitrate in dioxane are given in Table II and are shown graphically in Fig. 2 where log A is plotted against log c. Nine series of measurements were made in order to test the reproducibility of the results and the reliability of the methods. In the first three series covering the dilute region, the conductance at concentrations below 10^{-4} was somewhat erratic; this appeared to be due to impurities in the solvent, because the solvent conductance was about 4×10^{-13}. After re-treating the dioxane with sodium in liquid ammonia, and refluxing for about twenty hours over sodium–lead alloy, the solvent conductance was reduced to less than 2×10^{-14}. Measurements made in the dilute region with the re-treated dioxane gave consistent results. The conductance curve exhibited an unexpected complexity in structure,

TABLE II

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE

c	A	*c*	A	c	A
0.0_410	0.0_431	0.0_350	0.0_3129	0.015	0.0_3832
$.0_415$	$.0_428$	$.0_370$	.03162	.020	$.0_2125$
$.0_420$	$.0_427$	$.0_210$	$.0_3193$	.030	$.0_2261$
$.0_430$	$.0_427$	$.0_215$	$.0_3231$	.050	$.0_2958$
$.0_450$	$.0_430$	$.0_220$	$.0_3259$	.070	.0204
$.0_470$	$.0_434$	$.0_230$	$.0_3306$	.100	.0367
$.0_310$	$.0_4414$	$.0_250$	$.0_3376$	.150	.0596
$.0_315$	$.0_4526$	$.0_270$	$.0_3452$	.200	.0768
$.0_320$	$.0_4635$	.010	$.0_3569$	.300	.1005
$.0_330$	$.0_4861$				

but repeated determinations with different cells and with different methods of changing concentration were in agreement. Later, a similar structure,

TABLE III

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

H_2O, % c	0.034 A	0.112 A	0.343 A	0.602 A	2 35 A
0.0_410	0.0_430	0.0_434	. . .	0.0_3150	0.0102
$.0_415$	$.0_429$	$.0_433$	.....	$.0_3133$	$.0_2852$
$.0_420$	.0428	$.0_433$	0.0461	$.0_3124$	$.0_2745$
$.0_430$	$.0_429$	$.0_434$	$.0_460$	$.0_3115$	$.0_2618$
$.0_450$	$.0_433$	$.0_438$	.0460	.03108	$.0_2496$
$.0_470$	$.0_437$	$.0_442$	.0462	$.0_3107$	$.0_2431$
$.0_310$	$.0_4442$	$.0_4485$	$.0_4670$	.03108	$.0_2374$
$.0_315$	$.0_4560$	$.0_4598$	$.0_4761$	$.0_3114$	$.0_2322$
$.0_320$	.04676	$.0_4708$	$.0_4863$	$.0_3123$	$.0_2292$
0_330	$.0_4902$	$.0_4930$	$.0_3109$	$.0_3143$	$.0_2261$
0_350	$.0_3132$	$.0_3138$	$.0_3156$	.03188	$.0_2231$
$.0_370$	$.0_3166$	$.0_3176$	$.0_3202$	$.0_3243$	$.0_2224$
$.0_210$	$.0_3204$	$.0_3225$	$.0_3272$	....	$.0_2227$
$.0_215$	$.0_3247$	....	$.0_3380$	....	....
$.0_220$	$.0_3279$	. .	. .	. . .	. . .

TABLE IV

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

H_2O, % c	0.331 Λ	1.242 Λ	4.01 Λ	6.37 Λ
0.0_415	.....	0.0_375	....	...
$.0_420$	.....	$.0_367$	....	...
$.0_430$	.....	$.0_358$	....	...
$.0_450$	0.0_457	$.0_348$	....	...
$.0_470$	$.0_460$	$.0_344$	....	...
$.0_310$	$.0_4649$	$.0_3403$	0.0452	0.596
$.0_315$	$.0_4742$	$.0_3376$	.0388	.494
$.0_320$	$.0_4840$	$.0_3368$	.0347	.433
$.0_330$	$.0_3105$	$.0_3368$	.0296	.363
$.0_350$	$.0_3152$	$.0_3398$	.0245	.310
$.0_370$	$.0_3202$	$.0_3442$	.0219	.256
$.0_210$	$.0_3272$	$.0_3525$	.0200	.225
$.0_215$	$.0_3372$	$.0_3697$	.0185	.197
$.0_220$	$.0_3457$	$.0_3894$	.0180	.182
$.0_230$	$.0_3593$	$.0_2131$	.0180	.167
$.0_250$	$.0_3794$	$.0_2220$	.0200	.158
$.0_270$	$.0_3992$	$.0_2323$	.0232	.161
.010	$.0_2133$	$.0_2495$	.0301	.175
.015	$.0_2207$	$.0_2844$	.0462	.214
.020	$.0_2309$	.0133	.0681	.266
.030	$.0_2646$	.0272	.128	.393
.050	.0200	.0675	.282	.684
.070	.....	.111	....	...
.100	.....	.168	.....	...

TABLE V

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

H_2O, % c	9.50 Λ	14.95 Λ	20.23 Λ	53.0 Λ	100 Λ
0.0_415	..	...	...	...	..
$.0_420$	..	...	...	...	..
$.0_430$	..	24.35	32.45	...	..
$.0_450$	5.46	22.75	31.70	...	..
$.0_470$	4.84	21.55	31.05	...	..
$.0_310$	4.22	20.10	30.25	...	..
$.0_315$	3.61	18.35	29.10	...	..
$.0_320$	3.23	17.10	28.15	41.75	..
$.0_330$	2.76	15.40	26.65	41.50	..
$.0_350$	2.27	13.40	24.60	41.15	85.1
$.0_370$	2.00	12.15	23.15	40.80	84.7
$.0_210$	1.76	10.95	21.65	40.40	84.3
$.0_215$	1.53	9.70	19.90	39.85	83.6
$.0_220$	1.40	8.95	18.75	39.35	83.1
$.0_230$	1.25	7.97	17.20	38.55	82.1
$.0_250$	1.13	6.95	15.30	37.40	80.6
$.0_270$	1.08	6.44	14.15	36.50	79.4
.010	1.07	6.05	13.05	35.45	..
.015	1.13	5.75	12.10	34.10	..
.020	1.22	5.64	11.60	33.00	..
.030	1.43	5.62	11.00	31.35	..
.050	1.88	5.78	10.45	29.10	..
.070	..	...	10.15	...	..
.100	..	...	...	...	..

namely, three inflection points in the moderately concentrated region, was obtained for other systems.

Conductance values for tetraisoamylammonium nitrate in various mixtures of dioxane and water are given in Tables III–V. Round concentrations c are given in the first columns and interpolated equivalent conductances A are given in the other columns. The weight percentages of water in the mixed solvents are given at the head of each conductance column. The solvent conductances are given in the last column of Table XII. These mixtures correspond to solvents whose dielectric constants range from 2.2, that of dioxane,[9] to 78.6, that of water.[10] Table III covers the low range of dielectric constant, Table IV the intermediate range, and Table V includes the conductance in water. The conductance data for these mixtures are shown on a log c–log A plot in Fig. **3.** These curves will be discussed below but it may be pointed out here that at a concentration of 10^{-5} N the equivalent conductance changes over a million-fold as the dielectric constant of the solvent changes in the ratio of 2.2 to 78.6. It will be noted that minima appear in the conductance curves for low and intermediate values of the dielectric constant. The values of the minimum conductances and the corresponding concentrations are given in Table VI.

TABLE VI

MINIMUM CONDUCTANCES FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

% Water	$A_{min.}$	$N_{min.}$	% Water	$A_{min.}$	$N_{min.}$
0.112	0.0_4335	0.0_418	4.01	0.0178	0.0_225
.343	$.0_4595$	$.0_440$	6.37	.159	$.0_250$
.602	$.0_3107$	$.0_480$	9.50	1.07	$.0_290$
1.242	$.0_3364$	$.0_325$	14.95	5.60	.025
2.35	$.0_2224$	$.0_370$			

In order to find whether any of the characteristics of the curves were specifically due to water, the conductance of tetraisoamylammonium nitrate was determined in ethylene dichloride and in a mixture of ethylene

TABLE VII

TETRAISOAMYLAMMONIUM NITRATE IN ETHYLENE DICHLORIDE

c	A	c	A	c	A
0.0_450	50.1	0.0_210	22.9	0.015	10.45
$.0_470$	47.1	$.0_215$	20.2	.020	9.90
$.0_310$	43.6	$.0_220$	18.4	.030	9.40
$.0_315$	39.6	$.0_230$	16.15	.050	8.90
$.0_320$	36.8	$.0_250$	13.80	.070	8.65
$.0_330$	33.0	$.0_270$	12.50	.100	8.40
$.0_350$	28.4	.010	11.45	.150	8.20
$.0_370$	25.6				

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(9) J. W. Williams, THIS JOURNAL, **52**, 1831 (1930).

(10) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

TABLE VIII

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–ETHYLENE DICHLORIDE (22.9% $C_2H_4Cl_2$)

c	A	c	A	c	A
$0.0_{5}30$	0.0638	$0.0_{4}50$	0.0168	$0.0_{3}50$	0.0086
$.0_{5}50$	.0496	$.0_{4}70$	.0147	$.0_{3}70$	.0084
$.0_{5}70$	.0417	$.0_{3}10$	.0129	$.0_{2}10$	.0086
$.0_{4}10$	.0350	$.0_{3}15$	.0112	$.0_{2}15$	.0093
$.0_{4}15$	.0286	$.0_{3}20$	.0103	$.0_{2}20$	.0103
$.0_{4}20$	.0251	$.0_{3}30$	.0093	$.0_{2}30$	.0126
$.0_{4}30$	.0209				

dichloride and dioxane with a dielectric constant of 2.45. Walden's[11] value for the dielectric constant of ethylene dichloride is 10.4. These results are given in Tables VII and VIII.

Tetraisoamylammonium thiocyanate, which is much more soluble in benzene than the nitrate, was next investigated in order to permit a com-

TABLE IX

TETRAISOAMYLAMMONIUM THIOCYANATE IN DIOXANE, IN BENZENE AND IN BENZENE–ETHYLENE DICHLORIDE (13.13% ETHYLENE DICHLORIDE)

c	Dioxane A	Benzene A	Mixture A
$0.0_{4}10$	.....	.....	$0.0_{2}254$
$.0_{4}15$	.....	.....	$.0_{2}219$
$.0_{4}20$	$0.0_{4}34$	$0.0_{4}95$	$.0_{2}198$
$.0_{4}30$	$.0_{4}34$	$.0_{3}100$	$.0_{2}180$
$.0_{4}50$	$.0_{4}37$	$.0_{3}133$	$.0_{2}170$
$.0_{4}70$	$.0_{4}40$	$.0_{3}172$	$.0_{2}170$
$.0_{3}10$	$.0_{4}455$	$.0_{3}232$	$.0_{2}176$
$.0_{3}15$	$.0_{4}560$	$.0_{3}328$	$.0_{2}189$
$.0_{3}20$	$.0_{4}666$	$.0_{3}412$	$.0_{2}207$
$.0_{3}30$	$.0_{4}882$	$.0_{3}530$	$.0_{2}245$
$.0_{3}50$	$.0_{3}136$	$.0_{3}661$	$.0_{2}331$
$.0_{3}70$	$.0_{3}187$	$.0_{3}733$	$.0_{2}422$
$.0_{2}10$	$.0_{3}257$	$.0_{3}810$	$.0_{2}544$
$.0_{2}15$	$.0_{3}347$	$.0_{3}898$	$.0_{2}725$
$.0_{2}20$	$.0_{3}417$	$.0_{3}967$	$.0_{2}868$
$.0_{2}30$	$.0_{3}532$	$.0_{2}110$	.0111
$.0_{2}50$	$.0_{3}735$	$.0_{2}137$	.0153
$.0_{2}70$	$.0_{3}936$	$.0_{2}171$	.0195
.010	$.0_{2}129$	$.0_{2}237$	.0260
.015	$.0_{2}209$	$.0_{2}400$	.0385
.020	$.0_{2}331$	$.0_{2}634$	.0519
030	$.0_{2}712$	.0130	.0794
.050	.0199	.0257	.1274
.070	.0347	.0351	.....
.100	.0617	.0463	.....

TABLE X

TRI-ISOAMYLAMMONIUM PICRATE IN ETHYLENE DICHLORIDE, IN BENZENE, AND IN BENZENE-ETHYLENE DICHLORIDE (21.2% ETHYLENE DICHLORIDE)

c	Ethylene dichloride A	Benzene A	Mixture A
$0.0_{3}10$	....	.....	$0.0_{3}140$
$.0_{3}15$	....	.....	$.0_{3}114$
$.0_{3}20$	0.842	.....	$.0_{4}987$
$.0_{3}30$	.700	.....	$.0_{4}813$
$.0_{3}50$	.556	.....	$.0_{4}654$
$.0_{3}70$	.475	.....	$.0_{4}577$
$.0_{2}10$	.403	$0.0_{6}269$	$.0_{4}517$
$.0_{2}15$	.335	$.0_{6}288$	$.0_{4}472$
$.0_{2}20$	.293	$.0_{6}324$	$.0_{4}452$
$.0_{2}30$	.244	$.0_{6}408$	$.0_{4}442$
$.0_{2}50$	.194	$.0_{6}624$	$.0_{4}455$
$.0_{2}70$	.168	$.0_{6}925$	$.0_{4}490$
.010	.1430	$.0_{5}154$	$.0_{4}556$
.015	.1220	$.0_{5}311$	$.0_{4}708$
.020	.1098	$.0_{5}550$	$.0_{4}908$
.030	.0985	$.0_{4}140$	$.0_{3}143$
.050	.0903	$.0_{4}566$	$.0_{3}320$
.070	.0891	$.0_{3}159$	$.0_{3}628$
.100	.0903	$.0_{3}507$	$.0_{2}140$
.150	.0973	.....	.....
.200	.1136	.....	.....
.300	.1310	.....	.....

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(11) Walden, Z. *physik. Chem.*, **70**, 569 (1909).

parison of conductance values in different solvents of very low dielectric constant. Interpolated conductance data are given in Table IX for solutions of the thiocyanate: in dioxane, column 2; in benzene, column **3** and in a mixture of benzene and ethylene dichloride, with a dielectric constant of 2.8, column 4.

It was considered desirable, for purposes of comparison, to determine the characteristics of the conductance curve of a weak salt. Accordingly, tri-isoamylammonium picrate was investigated in benzene, in ethylene dichloride and in a mixture of these solvents having a dielectric constant of 3.1. The results are given in Table X.

The temperature coefficient of the conductance of tetraisoamylammonium nitrate in dioxane was determined at several concentrations, over the temperature range 18–35°. The results are summarized in Table XI. The concentration M for each series is given as moles of salt per kilo of solvent, and may be converted to normality by means of the equation

$$d = 1.029 - 0.0248\,M - 0.00105\,(t - 25°)$$

where d is the density, M weight concentration and t the temperature. The temperature coefficients are all positive, and decrease with increasing temperature. They depend markedly on concentration: the average

TABLE XI

TEMPERATURE COEFFICIENTS FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE

t, °C.	$\Lambda \times 10^4$	$100\,\Delta \log \Lambda/\Delta t$	t, °C.	$\Lambda \times 10^4$	$100\,\Delta \log \Lambda/\Delta t$
	M = 0.001064			M = 0.01038	
18.40	1.573		18.58	4.35	
		1.91			2.48
23.93	2.005		23.80	5.87	
		1.71			2.29
29.49	2.497		29.29	7.84	
		1.62			2.22
34.95	3.061		34.75	10.37	
	M = 0.002313			M = 0.0557	
18.36	2.072		18.76	98.5	
		2.23			1.99
23.91	2.755		23.96	125	
		2.10			1.90
29.47	3.606		29.50	159	
		1.91			1.76
34.80	4.557		34.65	196	
	M = 0.00773			M = 0.1111	
18.42	3.43		18.53	334	
		2.51			1.61
23.81	4.68		23.50	402	
		2.28			1.55
29.31	6.26		29.55	499	
		2.18			1.47
34.85	8.25		34.71	550	

value of $A \log \Lambda/\Delta t$ has a maximum at about 0.02 N, from which it decreases slowly toward higher and rapidly toward lower concentrations.

For purposes of comparison, the dielectric constants of the various mixtures together with those of the pure solvents are given in Table XII.[12]

TABLE XII

DIELECTRIC CONSTANTS

Composition of solvent $C_4H_8O_2$	 H_2O	Dielectric constant	Solvent conductance
100.0	0.0	2.20	$0.0_{13}2$
99.89	.112	2.25	$.0_{13}3$
99.66	.343	2.3	$.0_{13}5$
99.40	.602	2.4	$.0_{13}5$
98.76	1,242	2.6	$.0_{12}2$
97.65	2.35	2.9	$.0_{11}8$
95.99	4.01	3.5	$.0_{9}2$
93.63	6.37	4.4	$.0_{8}28$
90.50	9.50	5.8	$.0_{7}44$
85.05	14.95	9.0	$.0_{6}17$
79.77	20.23	12	$.0_{6}30$
47.0	53.0	37	$.0_{6}90$
0.0	100.0	78.6	$.0_{5}25$
$C_4H_8O_2$	$C_2H_4Cl_2$		
77.13	22.87	2.45	$.0_{11}65$
0.00	100.0	10.4	$.0_{9}3$
C_6H_6	$C_2H_4Cl_2$		
100.0	0.0	2.28	$.0_{13}1$
86.87	13.13	2.8	$.0_{12}1$
78.76	21.24	3.1	$.0_{11}43$

V. Discussion

The conductance of tetraisoamylammonium nitrate in dioxane is shown graphically in Fig. 2, where the logarithms of equivalent conductance and of concentration are plotted as ordinates and abscissas, respectively. This curve is typical of solutions of strong electrolytes in solvents of very low dielectric constant. The conductivity falls off continuously, although at varying rate, to concentrations well below 10^{-4} N. Indeed, if measurements had been carried only to this concentration, it might have been inferred that the conductance was approaching zero as the limiting value. Actually, however, below 10^{-4} *N*, the rate of decrease diminishes and there is evidence of a minimum in the conductance curve in the neighborhood of 2×10^{-5} *N*. What form the conductance curve may have at concentrations below the minimum point in the solvents of lowest dielectric constant could not be ascertained by the method employed in this investigation. Measurements in solvents of slightly higher dielectric constant, however,

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[12] For the dielectric constants of the mixtures, we are indebted to Mr. G. S. Hooper, of this Laboratory, who kindly carried through a series of measurements for us.

indicate that, after passing through a minimum point, the conductance increases with decreasing concentration in regular manner.

The curve at higher concentration is quite complex, since it exhibits three inflection points. The decreasing slope of the curve with increasing concentration at high concentrations may be accounted for on the assumption that the ion mobilities are decreasing, owing to the rapidly increasing viscosity of the solutions. Although the viscosities were not measured, it was quite evident that the viscosity of these solutions increases rapidly with increasing concentration. The complex structure of the remainder of the curve remains unaccounted for. Such a structure is seemingly found only in the case of the strongest electrolytes and is not dependent upon the particular solvent employed, so long as the dielectric constant is sufficiently low. Thus, a similar curve is found for tetraisoamylammonium thiocyanate in dioxane (Fig. 4, Curve V) and for the same salt in benzene (Fig. 4, Curve IV). On the other hand, a weaker electrolyte, tri-isoamylammonium picrate, yields a curve in which inflection points are absent (Fig. 5, Curve V).

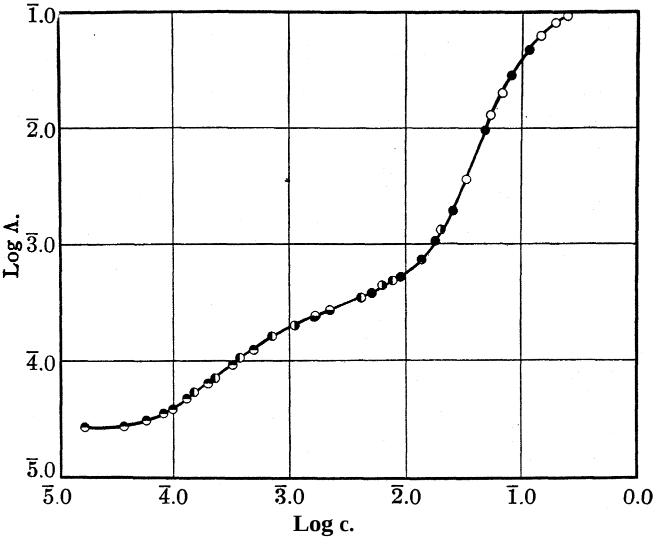

Fig. 2.—Tetraisoamylammonium nitrate in dioxane.

Incidentally, it may be pointed out that conductance values as determined by the alternating and by the direct current method are in excellent agreement. In Fig. 2, the open circles represent points determined by the alternating current method, while the other circles represent points determined by the direct current method. The black circles and the various half-shaded circles represent independent series of direct current measurements in which the methods of carrying out the dilution were varied. As may be seen from the figure, the various determinations are consistent. We may conclude, therefore, that the direct current method yields reliable results and that, even in solvents of dielectric constant as low as 2.2, the conductance curve passes through a minimum at very low concentration.

The influence of the dielectric constant of the solvent medium as well as the influence of specific factors upon the conductance of solutions is of considerable interest. By the methods employed, it was possible to extend the measurements to concentrations sufficiently low to permit determination of the general course of the curve at concentrations below the minimum point. This is well illustrated in Fig. **3** for solutions of tetraisoamylammonium nitrate in varying mixtures of dioxane and water. Dioxane was purposely selected as solvent, since it is completely miscible with water and thus permits of a continuous increase of the dielectric constant of the medium from that of dioxane, 2.2, to that of water 78.6. The composition of various mixtures in weight percentages of water is indicated on the figure.

It will be seen from the figure that, on addition of water to dioxane, the conductance is increased and the complex structure of the curve at higher concentration becomes less pronounced and ultimately disappears. The eccentricities in the conductance curve at higher concentration, while still noticeable at a concentration of 1.24% of water, have disappeared when the concentration of water reaches 4.0%. In the meantime, the minimum point has shifted toward higher concentration, namely, from 2 × 10^{-5}, in pure dioxane (D = 2.2)) to **3** × 10^{-3} N at 4% of water (D = **3.5**). As the dielectric constant of the medium increases with increasing concentration of water, the minimum point shifts more and more toward higher concentration and becomes less and less pronounced in that the approach from the high concentration side becomes less steep. **It** ultimately disappears for a mixture containing 20% of water (D = 12). The form of the conductance

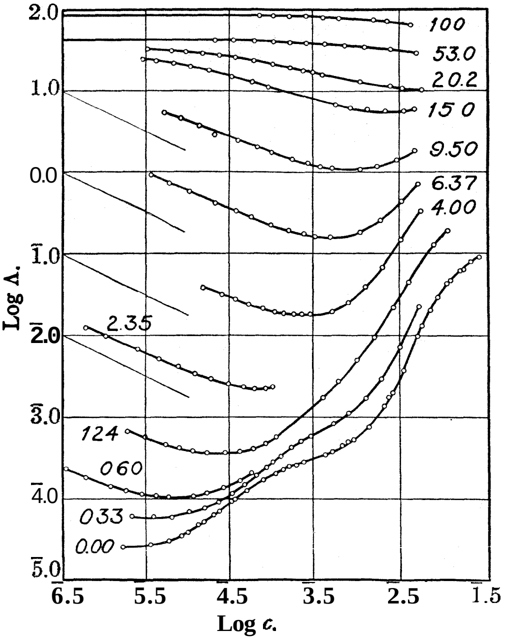

Fig. 3.—Tetraisoamylammonium nitrate in dioxane–water mixtures. (Weight per cent. of water given opposite corresponding curve.)

curve beyond the minimum point (toward lower concentration) remains unchanged as the dielectric constant increases and is practically linear on a logarithmic plot. For mixtures having dielectric constants above 12, the conductance curves are displaced chiefly by an increase of conductance in the more concentrated region and the curves approximate those of strong electrolytes in water.

There is no sharp shift in the conductance curve on the initial addition of water. The controlling factor seems to be the dielectric constant of the medium, for the form of the curves and the value of the conductance at a given concentration is practically the same whether the change in dielectric constant is brought about by the addition of water or of ethylene dichloride.

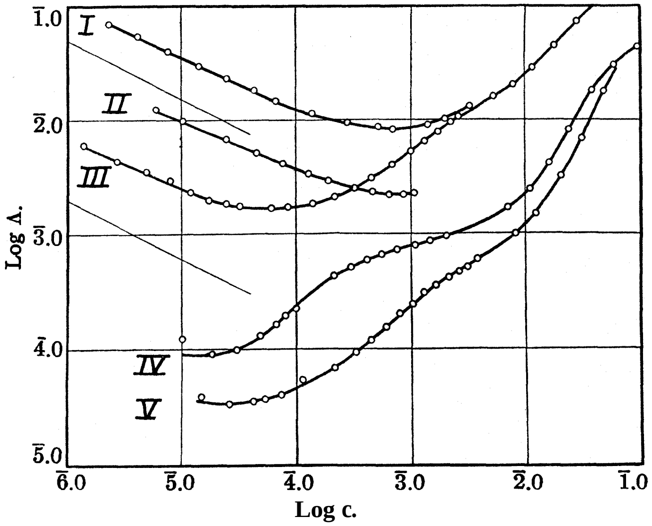

Fig. 4.—I, Tetraisoamylammonium nitrate in dioxane containing 22.9% ethylene dichloride; II, tetraisoamylammonium nitrate in dioxane containing 2.35% water; III, tetraisoamylammonium thiocyanate in benzene containing 13.13% ethylene dichloride; IV, tetraisoamylammonium thiocyanate in benzene; V, tetraisoamylammonium thiocyanate in dioxane.

This is well illustrated in Fig. 4, Curves I and II. The first curve is that of solutions of tetraisoamylammonium nitrate in a mixture of dioxane and ethylene dichloride ($D = 2.45$) and the second in a mixture of dioxane and water ($D = 2.9$). Both curves have a minimum point in the neighborhood of 10^{-3} N and both curves are practically linear and parallel at lower concentrations. The ethylene dichloride mixture is a considerably better conductor than the water mixture, but this is in a large measure due to the much lower viscosity of the former mixture. Curve III, Fig. 4, is for tetraisoamylammonium thiocyanate in an ethylene dichloride–benzene mixture, of dielectric constant 2.8, and it will be noted that the curve approximates that of tetraisoamylammonium nitrate in a dioxane–water mixture, of dielectric constant 2.6 (Curve 1.24, Fig. 3), except for a vertical displacement, presumably due to the difference in solvent viscosities. Curves IV and V, Fig. 4, represent the conductance of tetraisoamylammonium thiocyanate in benzene and dioxane, respectively. The structure of the two curves is much the same and, at low concentrations, the conductance values in the more fluid benzene are the higher. Quite unexpectedly, therefore, specific influences due to the solvent medium are absent, if we leave out of account viscosity effects.

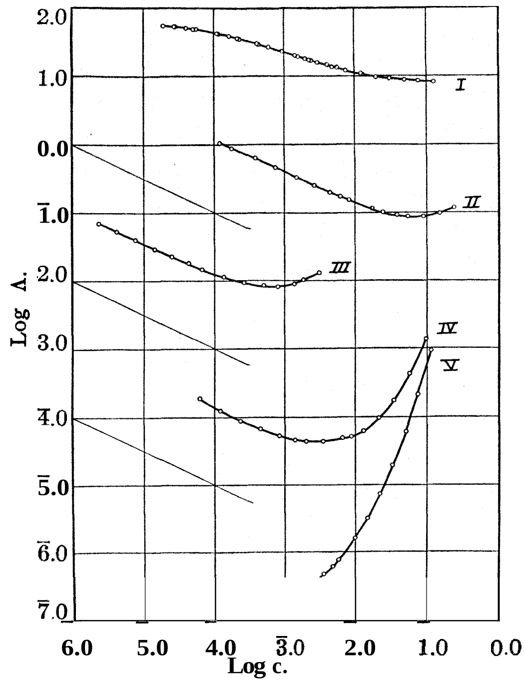

Fig. 5.—I, Tetraisoamylammonium nitrate in ethylene dichloride; II, tri-isoamylammonium picrate in ethylene dichloride; III, tetraisoamylammonium nitrate in dioxane containing 22.9% ethylene dichloride; IV, tri-isoamylammonium picrate in benzene containing 21.2% ethylene dichloride; V, tri-isoamylammonium picrate in benzene.

The conductance curve of tri-isoamylammonium picrate, a weak electrolyte, differs markedly from that of strong electrolytes. This will be evident on comparing Curve V, Fig. 5, for this electrolyte in benzene with Curves IV and V, Fig. 4, for tetraisoamylammonium thiocyanate in benzene and dioxane or with the curve for tetraisoamylammonium nitrate in dioxane, Fig. 2. It will be noted that the conductance of tri-isoamylammonium picrate in benzene is far below that of tetraisoamylammonium thiocyanate in the same solvent at corresponding concentrations. Thus, at 10^{-3} N, the conductance of the first electrolyte in benzene is approximately 2.5×10^{-7}, while that of tetraisoamylammonium thiocyanate is 10^{-3}. As the dielectric constant of the solvent medium is increased by adding ethylene dichloride to benzene, the conductance is largely increased. This is evident on comparing Curve V, Fig. 5, with Curve IV, Fig. 5, where the solvent contains 21% of ethylene dichloride ($D = 3.1$).

The difference in the behavior of a quaternary and a ternary salt at higher dielectric constant is well illustrated by Curves I and II, Fig. 5, for tetraisoamylammonium nitrate and for tri-isoamylammonium picrate, respectively, in ethylene dichloride. Curve III, for tetraisoamylammonium nitrate in a dioxane mixture containing 23% of ethylene dichloride, lies far above Curve IV, for the picrate in benzene containing 21% of ethylene dichloride. The dielectric constants of the solvents are, respectively, 2.45 and 3.1. As in the case of the strong salts, however, the minimum for the tertiary ammonium picrate shifts to higher concentrations with increasing dielectric constant and, at the same time, the slope of the curve, toward higher concentration, decreases. This phenomenon is characteristic of the transition from solvents of low to those of high dielectric constant.

One of the striking results of this investigation, best illustrated in Fig. 3 but also evident from Figs. 4 and 5, is the fact that, at concentrations below the minimum point, the curves as plotted are approximately parallel until the conductance reaches a value in the neighborhood of 1.0. This is illustrated in Fig. 3 by the curves for mixtures containing from 0.60 to 9.50% of water, as well as by Curves II, III and IV of Fig. 5 and Curves I, II and III of Fig. 4. The slope of the curves toward lower concentrations approaches a value of approximately minus 0.5, which is indicated by the straight lines drawn in the figures. Since, in the figures, logarithms of the equivalent conductance are plotted against logarithms of the concentration, it follows that the curves conform approximately to a simple equation $\mathrm{A} = A/C^{1/2}$, where A is constant. One should expect such a relation for a binary electrolyte if the conductance were determined by ionization according to the law of mass action. A theoretical discussion of the foregoing and other results is reserved for a future paper.

Summary

1. The conductances at 25° of the following systems have been determined over the concentration range 0.2–0.00001 N: tetraisoamylammonium nitrate in dioxane, water, ethylene dichloride and various mixtures of ethylene dichloride and of water with dioxane; tetraisoamylammonium thiocyanate in dioxane, benzene and a mixture of benzene and ethylene dichloride; and tri-isoamylammonium picrate in ethylene dichloride, benzene and a mixture of these two solvents.

2. It is shown that, at sufficiently low concentrations, the equivalent conductance increases with dilution, even in solvents of very low dielectric constant.

3. The influence of the dielectric constant on conductance has been determined over the range from dioxane to water and it has been found that, viscosity excepted, specific influences due to the solvents are not conspicuously present.

4. The behavior of strong and weak electrolytes is compared.

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The Entropy of Polyatomic Molecules and the Symmetry Number

BY JOSEPH E. MAYER, STEPHEN BRUNAUER AND MARIA GOEPPERT MAYER

Introduction

The calculation of the entropy of organic gases from molecular structure data promises considerable aid to the physical chemistry of organic compounds. Vapor pressure data and heats of vaporization are usually available and accurate estimations of the entropies of the gases may be used easily to calculate the entropies of the solid and liquid states. With heats of combustion these data can be used to calculate free energies and to estimate equilibria.

Calculations of the specific heats and entropies of diatomic molecules from spectral data have long been made, and have yielded results of great accuracy.[1]

More recently Villars and Schultze,[2] Villars,[3] Giauque and his students,[4,5] and Sterne[6] have used similar methods to calculate the entropies of some polyatomic molecules.

The method depends on the empirical fact that the energy of the single molecule may be fairly accurately accounted for as the sum of several independent terms. These terms are the translational energy, the energy due to rotation with constant moments of inertia, and the energies of one or more harmonic vibrational degrees of freedom. In the language of the quantum mechanics this condition is that the correct function necessary to represent any state of the molecule at low energies ($\epsilon/kT \sim 1$) be given to a good approximation as a product of independent functions of the various coordinates, and, further, that the potential energy be a sum of squares of the vibrational coordinates. If the above conditions hold, the entropy may be separated into additive terms due to translation, rotation, vibration, nuclear spin and to electron degeneracy. It is assumed that the lowest electron excitation has a high energy compared to kT and contributes nothing to entropy or specific heat. It is also convenient to make use of the fact that, with the possible exception of hydrogen, the moments of inertia of all actual molecules are so large that the entropy of rotation is given accurately by the classical equation at temperatures of about 200–300°K.

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[1] See for instance Giauque, THIS JOURNAL, 52, 4816 (1930); 53, 507 (1931).

[2] Villars and Schultze, *Phys. Rev.*, 38, 998 (1931).

[3] Villars, *ibid.*, 38, 1552 (1931).

[4] Giauque, Blue and Overstreet, *ibid.*, 38, 196 (1931).

[5] MacDougall, ibid., 38, 2074 (1931).

[6] Sterne, *Phys. Rev.*, 39, 993 (1932).

The fundamental equations for the more general case are given by Giauque.[7] If the above conditions hold the molar entropy of a diatomic gas of unlike atoms may be expressed as

$$S = R\left[\ln \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{5/2}\left(\frac{8\pi^2IkT}{h^2}\right) e\, p_e p_n + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln\left(1 - e^{-h\nu/kT}\right)\right] \tag{1}$$

where R is the gas constant, V is molar volume, N is Avogadro's number, m is $m_1 + m_2$, the mass per molecule, k $= R/N$, the Boltzmann constant, h is Planck's constant, e = 2.7183, base of natural logarithms, $I = \mu r^2$ $[\mu = m_1m_2/(m_1 + m_2)]$, the moment of inertia, ν is the frequency of vibration, p_e is the degeneracy of the lowest electronic level, p_n is the degeneracy due to nuclear spin

$$p_n = (2s_1 + 1)(2s_2 + 1)$$

where s_1 and s_2 are the spins of atoms 1 and 2. We express the entropy divided by R at temperature T of the harmonic vibrator of frequency ν as

$$S_{\mathrm{Ein}}(\nu, T) = \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln\left(1 - e^{-h\nu/kT}\right) \tag{2}$$

which, when $h\nu/kT$ is equal to about four or greater, becomes approximately

$$S_{\mathrm{Ein}}(\nu, T) \cong (h\nu/kT + 1)e^{-h\nu/kT} \tag{3}$$

Equation (1) can then be written for 1 atm. pressure

$$S = R\left[0.769 + \frac{7}{2}\ln T + \frac{3}{2}\ln W + \ln A' + \ln p_e + \ln p_n + S_{\mathrm{Ein}}(\nu, T)\right] \tag{4}$$

where W is molecular weight and $A' = I \times 10^{38}$.

The nuclear spin entropy $R \ln p_n$ may in practice be omitted. Gibson and Heitler[8] have shown that it does not alter in any reaction involving diatomic molecules, and it is usually assumed that this is also true for polyatomic molecules. The results of this paper prove that this is actually the case.

If the two atoms of the diatomic molecule are identical. or if we deal with a polyatomic molecule with two or more identical atoms, a new difficulty arises. Certain rotation states may not occur, or may occur only for molecules with a definite nuclear spin. Essentially the same problem has been handled with the methods of the classical statistics by Ehrenfest and Trkal.[9] They showed that $R \ln a$ must be subtracted from any entropy equation like the above, in which a, the symmetry number, represents the number of permutations of like atoms which can be carried out by changes in the coordinates of rotation alone (nuclear spin neglected). That is, a is the number of ways in which the molecule can be rotated and still look identical. The argument is essentially the same as that which

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[7] Giauque, This Journal, 52,4808 (1931).

[8] Gibson and Heitler, *Z. Physik*, 49, 465 (1928).

[9] Ehrenfest and Trkal, *Proc.* Sect. *Sci. Amsterdam*, 23, 169 (1920).

justified the division of the total phase space of a gas of N identical molecules by N!, the number of permutations which left the system unchanged.

Hund[10] has discussed the quantum mechanical method by which one can determine the allowed rotational states for a molecule of definite nuclear spin type. **Elert**[11] has applied **Hund's** method to methane, and Villars and Schultze,[2] and Villars[3] have used the results of Hund and Elert to make detailed calculations of the entropies of methane and ammonia. Giauque[4] has correctly pointed out that at room temperatures the entropies of these gases must be given by the usual formulas with terms for classical rotational entropies minus R ln a.

There exists, however, no proof consistent with the formal quantum mechanical derivation of statistics which shows that such a procedure may be universally applied. This is proved here for all molecules with one a'-fold axis and a perpendicular plane of symmetry or lower symmetry. Since probably the only molecules of higher symmetry are tetrahedral (methane like), and it follows from the work of Elert that the symmetry number may be used for these, the procedure can be used generally.

In addition the quantum mechanical solution is given for a symmetric top with two rigid bodies of equal moments of inertia independently rotating about the unique axis. This probably represents the best zeroth order approximation for the ethane molecule, in which it seems likely that there is nearly free rotation about the C–C bond. The equation for the energy levels is derived. The classical entropy of rotation of a gas composed of such molecules is calculated.

The Symmetry Number

We wish first to consider a system composed of N independent similar particles, that is, a system the energy function of which has no terms containing the coordinates or momenta of more than one particle. The functions Ψ giving the state of the system may be expressed as products $\Pi_{i=1}^{i=N}\ \psi_k(i)$. $\psi_k(i)$ is then a function of the coordinates (i) (including spin) of the i'th particle, k represents the value of all of the quantum numbers of the i'th particle. For any single function Ψ_l in which k for each particle is given, we shall introduce the integers λ_k giving the number of particles in the completely defined quantum state k. There will be $N!/\Pi_k\lambda_k!$ different functions having the same values of the λ_k's obtainable from each other by carrying out all of the permutations of particles which have different values of k. All these functions will be solutions to the original differential equations which, with the spin and boundary conditions, determined our system. They will be orthogonal to each other and we will assume them to be normalized. Therefore, any linear combination of these functions will be a solution.

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[10] Hund, *Z. Physik*, 43, 788; 43, 805 (1927).

[11] Elert, *ibid.*, 51, 6 (1928).

There is one other condition which any function expressing the state of the system must fulfil to be acceptable. If the particles contain an odd number of fundamental units, protons, electrons and probably neutrons, that is, if the particles have half integer spins, the function must be completely antisymmetric. This means that it must become multiplied by minus one by a single transposition of two particles, that is, a transposition of two identical groups of electrons and protons. If the particles contain an even number of units, have zero or integer spins, the function must be completely symmetric, it must be unchanged by a transposition. (A function antisymmetric in transpositions of electrons, protons (and neutrons) would be symmetric in the transposition of two identical groups of an even number of such units, for example, two carbon nuclei.)

There is only one linear combination of all the $N!/\Pi_k\lambda_k!$ functions having the same λ_k values which is perfectly symmetric and normalized, namely, the sum of all the functions. There is only one linear combination which is antisymmetric, the sum of all N possible permutations, the even permutations taken with positive, the odd with negative signs. This antisymmetric function will be identically zero if any λ_k is greater than 1. These two cases of symmetric and antisymmetric functions correspond to the Bose–Einstein and Fermi–Dirac statistics, respectively. In each case a single state is defined by the integers λ_k, and in the second case only values 1 or 0 are allowed.

We are interested in a molecule composed of several atoms of which a certain number may be identical. Since in this case the potential energy is not independent of the relative positions of the atoms (indeed it depends only on the relative positions), we cannot make even an approximate solution in terms of products of functions of the atomic coordinates. We can, however, transform to such coordinates that, to a good approximation, the complete function Ψ of the molecule may be expressed as a product of functions of these coordinates. These coordinates which have no interaction terms are the familiar natural coordinates of translation, rotation and the classical normal coordinates of vibration, as well as the coordinates of nuclear spin which remain untransformed.

The nuclear position coordinates and the natural coordinates must be connected by transformation equations such that the values of one set completely define all the values of the other set. We will find in general that there are several values of the relative positions of the atoms which will have identical minimum values of the potential energy. These will correspond to what will be called here different "optical isomers," according to the terminology of Hund. It is to be understood that among these optical isomers may occur members that differ only in the permutation of identical atoms and will not differ in light rotating power. These positions of minimum energy will all correspond to the same zero value of all the vibrational coordinates. It is necessary, then, to add an extra coordinate to our natural system, the value of which tells us in what optically isomeric form our system is. This coordinate i, by definition, may take only a finite number of discrete values a, b, ... n, corresponding to the n isomers. The eigenfunctions of this coordinate will be $\psi_c(i) = \delta(ci)$, $\delta(ci) = 1$ when $i = c$, $\delta(ci) = 0$ when $i \neq c$, in which c designates the Isomeric state of the molecule.

The complete function Ψ of the molecule may be expressed as a product of the type

$$\Psi = \psi\,(\text{electron}) \times \psi\,(\text{isomer}) \times \psi\,(\text{vibration}) \times \psi\,(\text{rotation}) \times \psi\,(\text{nuclear spin}) \times \psi\,(\text{translation})$$

We shall assume that the function ψ (electron) has been completely solved, and that it is symmetrical to transpositions of identical nuclei, which is usually the case with stable chemical compounds. The following argument is made simpler by this assumption, although the conclusions are independent of it. ψ (translation) depends only on the coordinates of the center of gravity which are unaffected by transpositions of like nuclei and it is therefore perfectly symmetrical. The normal coordinates of vibration may be so selected that they are either unaffected, or change sign, when two like nuclei are transposed. The lowest energy eigenfunction of a harmonic oscillator is symmetric to a change of sign of the coordinate, as are all states with even quantum numbers. In the lowest vibrational energy level ψ (vibration) is then symmetrical. As in the case of ψ (electron) the conclusions we draw will also hold for higher non-symmetric vibration states, but the language of the discussion is simplified if we deal only with the symmetrical case.

The product of the three symmetrical functions ψ (electron) $\times$ ψ (vibration) $\times$ ψ (translation) will be symmetrical and therefore the complete function ψ will have the symmetry character of the remaining product, (or linear combination of the product), ψ (isomer) $\times$ ψ (rotation) $\times$ ψ (nuclear spin). This product must be antisymmetrical to transposition of atoms with half integer spins, and symmetrical to transpositions of atoms with integer or zero spins.

The symmetry number a of a molecule is defined as the number of permutations of identical particles in the molecule which can be carried out by changes in the coordinates of rotation and spin alone.

The Unsymmetrical Molecule.--If a = 1 the rotational coordinates will be unaffected by permutations and the rotational function ψ (rotation) will be perfectly symmetrical. If the molecule contains only N like atoms there will be N isomer functions. If the molecule contains several of each of two kinds of atoms or in general more kinds of atoms, there may exist physically distinguishable (light rotating) isomers of the same potential energy. We may then arbitrarily use two coordinates, one of which defines the physically indistinguishable optical isomer resulting from permutation of the like atoms, the other defines the physically distinguishable isomeric state. The complete isomer function will then be a product of functions of each of these two coordinates. The functions of the coördinate of distinguishable isomers, which do not contain the coordinate of the like atom permutations, will be symmetric to these permutations, and may be omitted from the discussion. The number of the other isomer functions will be N!

Not only simple products of isomer and spin functions will be solutions of the problem. Linear combinations of the isomer functions multiplied by linear combinations of the spin functions will also be solutions, and any linear combinations of permutations of these products. We seek the number of such orthogonal functions which fulfil the conditions of perfect symmetry (/antisymmetry). The *exact* solution of the complete function Ψ is not a product of functions of the different coordinates, since there are actually small interaction terms. Nevertheless, the true Ψ may be determined by the method of perturbations from such a product. It will have the same symmetry character as the product, provided we use the correct zeroth order function of the many possible linear combinations which satisfy the degenerate problem. For any physical perturbation, since it must be symmetrical in identical particles, the correct linear combinations of isomer and spin functions are a complete set of representatives of all the possible symmetry characters.

Using the group theory Wigner[12] has discussed this general problem, **Hund**[13] has recapitulated the discussion and the results without the use of the group theory.

A function of N identical particles is said to belong to the symmetry character $S(\lambda_1 + \lambda_2 + \ldots + \lambda_j + \ldots + \lambda_n)$ with $\Sigma_j \lambda_j = N$ and $\lambda_j \geq \lambda_{j+1}$ if it cannot be made by permutation and linear combination symmetric in more than X_1 particles, and by permutation of the remaining $N - \lambda_1$ particles symmetric in more than λ_2 particles, etc. A *representative* of this symmetry character is symmetric in one group of λ_1 particles, and in another of λ_2 particles, etc.

Any function of symmetry character $\tau = S(\lambda_1 + \lambda_2 + \ldots + \lambda_j + \ldots + \lambda_n)$ has a degeneracy n_τ where $n_\tau = N! \, \Pi_{j>l}(\lambda_l - \lambda_j + j - l)/\Pi_j(\lambda_j + n - j)!$ If the system has no degeneracy besides that due to the identity of the particles, there are n_τ different functions of character τ each having a degeneracy n_τ making in all n_τ^2 orthogonal functions, with $\Sigma_\tau n_\tau^2 = N!$

To every symmetry character τ there corresponds another character τ^* called the reciprocal character[14] and $n_{\tau^*} = n_\tau$. The degeneracy of a

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[12] Wigner, *Z. Physik*, 40, 492 (1926); 40, 883 (1927).

[13] Hund, *ibid.*, 43, 788 (1927); 43, 805 (1927).

[14] **The definition of the reciprocal character is given by Hund.**[13]

product of functions of character τ and τ' is $n_\tau \times n_{\tau'}$. A symmetric (/antisymmetric) function can only be formed by permutation and linear combination from the product of two functions of characters τ and τ' if $\tau' = \tau (/\tau' = \tau^*)$, and then only the fraction $1/n_\tau^2$ of all the linear combinations leads to a symmetric (/antisymmetric) function.

Spin functions are generally degenerate because there are only $2s + 1$ possible functions per particle. The number of functions of character τ is not in general n_τ and may be zero, although the degeneracy of each existing function must be n_τ.

If the molecule is composed of N identical atoms of spin s there will be $(2s + 1)^N$ spin functions, from which linear combinations may be formed that can be classified into non-combining groups of different symmetry character. The $N!$ orthogonal isomer functions may also be formed into non-combining groups of different character, n_τ^2 functions of the character τ. Only products of isomer and spin functions belonging to the same (/reciprocal) character, may by permutation and linear combination lead to functions completely symmetric (/antisymmetric) to transpositions of identical atoms. From the product of n_τ spin functions of character τ with all the n_τ^2 isomer functions of character τ $(/\tau^*)$ only the fraction $1/n_\tau^2$ or n_s completely symmetric (/antisymmetric) functions can be formed. If we sum the symmetric (/antisymmetric) products over all the different nuclear spin symmetry characters, we obtain as many functions as the total number of nuclear spin functions, $(2s + 1)^N$.

The conclusion is that a molecule of symmetry number $\sigma = 1$, composed of N identical atoms of spin s will have $(2s + 1)^N$ orthogonal functions representing $(2s + 1)^N$ degenerate states for every value of the usual quantum numbers of the molecule. To the simple entropy expression for such a molecule must be added $RN \ln (2s + 1)$, or $R \ln (2s + 1)$ nuclear spin entropy for every atom of spin s.

Had the molecule contained other unlike atoms i, j of spin s_i, s_j the preceding argument could have followed in detail for each of the $\Pi_i(2s_i + 1)$ spin states of these atoms. To the entropy should then be added $R \ln (2s_i + 1)$ for every atom of spin s_i.

Had the number of unlike atoms been greater than 3 there may have been a number I of physically distinguishable isomers and the argument would lead to an additional entropy $R \ln I$.

If the molecule contained an additional N_k identical atoms k of spin s_k a similar grouping of functions with respect to the isomers obtained by permuting the atoms k, for every one of the preceding functions, would lead to an additional $RN_k \ln (2s_k + 1)$ in the entropy.

The total nuclear spin entropy $R \ln (2s_i + 1)$ for every atom of spin s_i is the same expression as that in monatomic and diatomic gases, and as will later be shown in symmetrical polyatomic molecules. This entropy will cancel in all chemical reactions and need not be included in any practical values. The entropy due to the **I** physically distinguishable isomers, R **ln I,** will not cancel, and must always be included.

Those isomers that are not physically distinguishable, that is, the isomers corresponding to different permutations of identical atoms, occur in the complete function of the molecule in the form of linear combinations. Due to the symmetry demands of the Pauli principle no molecule can be said to be composed of only one isomeric type. On those isomers which are physically distinguishable there are no such limitations. As far as present knowledge goes we may write a molecular function which contains only one isomer. Professor G. N. Lewis has suggested to one of us that even in the exact solution the different isomer functions may not combine. This certainly appears reasonable to the prejudice of the chemist, for otherwise not only would the two states have slightly differing energies, but a gas of one isomer cooled to such a temperature that excitation in a given time had low probability, would in finite time be transformed 100% into the other isomer! The mathematical reason for this probable intrinsic degeneracy is, however, not obvious.

The Symmetric Molecule.—In order to investigate the case of a molecule a > 1, ψ (rotation) must be considered. Only molecules having no higher symmetry than a σ'-fold axis of symmetry, and with or without a plane of symmetry perpendicular to this axis will be considered. For these cases a $= 2\sigma'$ or a = a', respectively. Since probably tetrahedral molecules are the only actual cases of a > 1 not falling into these classes the case is quite general. There will be $N!/\sigma$ different isomer functions, and a rotational functions, which latter we shall show differ only by a phase factor. All such molecules will either be symmetric top types, or sufficiently close to it to allow symmetric top eigenfunctions to be used as a first approximation. Higher approximations will show the same number of states, and the same symmetry characters as the zeroth

The rotational eigenfunctions of the symmetrical top problem have been solved in the usual Eulerian angles, θ, ψ and φ.[15,16]

The form of equation here used is given by Hund. The solutions may be written

$$\psi\ \textbf{(rotation)} = \begin{cases} v_{j,m,\lambda}\left(\sin\dfrac{\theta}{2}\right) e^{\pm i(m\psi + \lambda\varphi)} \\ \\ v_{j,m,\lambda}\left(\cos\dfrac{\theta}{2}\right) e^{\pm i(m\psi - \lambda\varphi)} \end{cases} \tag{5}$$

where $j \geq m \geq 0, j \geq \lambda \geq 0$

$$v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right) = \cos^s\frac{\theta}{2}\sin^d\frac{\theta}{2}\,F\left(\frac{s+d}{2} - j, 1+s+d,\ 1+d, \sin^2\frac{\theta}{2}\right)$$

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[15] Dennison, *Phys. Rev.*, 28, 318 (1926).

[16] Reiche, Z. *Physik*, 39, 444 (1926).

and $s = m + X$, $d = |m - \lambda|$. F is the Jacobi polynomial. The energy, if C is the moment of inertia about the unique axis and A is the moment about the other two axes, has the form

$$E = \frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)\lambda^2\right] \tag{6}$$

Of the permutations of identical atoms σ' lead only to a different phase of rotation about the axis of symmetry, the unique axis of the top, differences which in the natural coordinates correspond only to shift of the type in which φ changes to $\varphi + q2\pi/\sigma'$ where q is an integer. The only change in the complete function of the natural coordinates, without the spin coordinates, is multiplication by a complex number, (exp.)$i\lambda q2\pi/\sigma'$.

If the molecule has a plane of symmetry perpendicular to the unique axis the function is further degenerate. States differing in the substitution of cos $(\theta/2)$ for sin $(\theta/2)$ and simultaneously $-\varphi$ for φ will have identical energies even in the presence of a magnetic field, and even if the top is not perfectly symmetric. We may then rewrite and form the linear combinations

$$\psi\ (\text{rotation}) = \begin{cases} \left[v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right)e^{\pm i\lambda\varphi} + v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right)e^{\mp i\lambda\varphi}\right]e^{\pm im\psi} \\ \left[v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right)e^{\pm i\lambda\varphi} - v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right)e^{\mp i\lambda\varphi}\right]e^{\pm im\psi} \end{cases} \tag{7}$$

An end to end transformation of the unique axis corresponds to the following changes: θ to $\pi - \theta$, ψ to $\pi + \psi$, and φ to $-\varphi$. The first of the equations is multiplied by (exp.) $\pm im\pi$ by this change, the second by $-$(exp.) $\pm im\pi$, that is, since m is an integer, by ± 1 and ∓ 1.

The molecule of symmetry nhmber σ greater than one has then no longer N orthogonal products of isomer and rotation functions corresponding to the N! permutations. The permutations fall into $N!/\sigma$ groups, each containing σ permutations: the isomer times rotation functions for any of one group can be obtained from any of the other of that group by multiplication by a (complex) factor. There are only $N!/\sigma$ orthogonal functions for every value of the usual quantum numbers. The question is, can every symmetry character be formed out of these $N!/\sigma$ orthogonal functions as the quantum numbers change their values, and, if so, what will be the number of functions of the various symmetry characters?

We may write in a purely formal manner a complete set of orthogonal representatives of the symmetry characters as linear combinations of the various permutations. For each of these permutations must now be substituted the appropriate product of an isomer function and a rotational phase factor. The permutations belonging to each isomer may be grouped and the phases factored out as a sum, which, for instance, in the perfectly symmetrical case will have the form $\Sigma_{q=0}^{q=\sigma'-1}$(exp.)$i\lambda q2\pi/\sigma'$. The complete function may then be multiplied by a complex factor containing λ, such as (exp.) $-i\lambda q 2\pi/\sigma'$, if necessary, to assure that at least one of the phase factors contains 1 in the sum (in the symmetrical case the term with $q = 0$ is already 1). These functions are assuredly orthogonal and are representatives of various symmetry characters. Any one may, however, be identically equal to zero for any given value of the quantum numbers m and λ. The zero value will evidence itself by the fact that each of the phase factors, functions of m and X, will be zero. For every value of m and λ (and for each function of (7) and each j) there will be only $N!/\sigma$ functions which are other than zero.

The sum of all of the phase factors over all values of A between $a + 1$ and $a + \sigma'$ inclusive, and if the molecule contains a plane of symmetry, over an even and an odd value of m, may now be made for each function. Since at least one phase factor contains 1 the sum will not be zero because $\Sigma_{\lambda=a+1}^{\lambda=a+\sigma'}(\text{exp.})\lambda 2\pi i q/\sigma' = 0$, unless $q = 0$ or $q = \sigma'$. Every function exists at least once in these values of the quantum numbers m and A. Since the total number of orthogonal functions which can exist is a X $N!/\sigma$ $= N!$, and this is the number of all of our functions, every function exists exactly once. Over a range of σ' consecutive values of λ and two adjacent values of m the same functions exist, and the same number of them, as exist for every quantum state of a completely unsymmetric molecule.

Within the range of the quantum number λ between $a + 1$ and a + a' (and for two consecutive values of m if the molecule has a plane of symmetry) there are n_τ^2 isomer times rotation functions of character τ. We may then proceed as for the case when a $= 1$ to multiply each of these functions with the spin functions of the same (/reciprocal) symmetry character, and find $(2s + 1)^N$ completely symmetric (/antisymmetric) linear combinations of the products. We obtain for the above a rotation states just as many acceptable orthogonal normalized functions as were previously obtained for every single rotation state of the unsymmetric molecule.

The result allows us to make the following statement. For temperatures high enough that (exp.)$\delta\epsilon/kT$ is about equal to 1, where $\delta\epsilon$ is the energy difference between states having values of λ differing by a', the molar entropy of a molecule having a symmetry number a is R ln a less than the entropy of the same molecule were it entirely non-symmetrical.

It is also a corollary that every nuclear spin state exists in the same proportion as in a non-symmetrical molecule, and the entropy due to nuclear spin will be R ln $(2s + 1)$ for every atom of spin s.

The Ethane Like Top

It appears to be probable that single valence bonds show no potential energy changes in rotation. The opposite rotation of the two CH_3 groups in ethane about the C–C axis, for instance, would cause potential energy changes only due to the varying distances between hydrogen atoms. This effect cannot be very great. It seems reasonable to choose as the zeroth approximation for such a molecule the solutions for absolutely free rotation. Probably the states most numerously present in the gas at 200–300°K. will be given fairly accurately by functions obtained on the basis of this assumption. A3 model for the problem is then chosen a symmetrical top with two equal moments of inertia A about two perpendicular axes x' and y', and consisting of two similar rigid bodies of equal moments of inertia C. Each of the bodies can be independently rotated about the unique axis of the top z'. z' is then the axis of the C–C bond in ethane.

If p and q are the angular velocities about x' and y', and r_1 and r_2 the angular velocities of the bodies 1 and 2, respectively, about z', the kinetic energy will be

$$T = \frac{1}{2}\,[A(p^2 + q^2) + C(r_1^2 + r_2^2)]$$

Angles similar to the Eulerian angles are introduced. θ is the angle between the fixed z axis in space and z', + the angle between the nodal line of the xy and $x'y'$ planes and the fixed x axis, φ_1 and φ_2 the angles between the nodal line and two fixed axes in the two rigid bodies 1 and 2, respectively. Defining p_θ, p_ψ, p_{φ_1} and p_{φ_2} as the momenta conjugate to the respective coordinates, the equation for the kinetic energy may be written

$$T = \frac{1}{2}\left[\frac{p_{\theta}^2}{A} + \left(\frac{A}{C} + \cot^2\theta\right)\frac{p_{\varphi_1}^2 + p_{\varphi_2}^2}{A} + 2\cot^2\theta\,\frac{p_{\varphi_1}p_{\varphi_2}}{A} + \right.$$
$$\left.\frac{p_\psi{}^2}{\sin^2\theta\ A} \quad \frac{2\cos\theta\ p_\psi}{\sin^2\theta\ A}(\mathrm{PI} + p_{\varphi_2})\right] \qquad (8)$$

Transformation by the usual method yields the Schrodinger equation for ψ (rotation), which is here written U. The equation is

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial U}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 U}{\partial\psi^2} + \left(\frac{A}{C} + \cot^2\theta\right)\left(\frac{\partial^2 U}{\partial\varphi_1^2} + \frac{\partial^2 U}{\partial\varphi_2^2}\right) +$$
$$2\cot^*\theta\,\frac{\partial^2 U}{\partial\varphi_1\partial\varphi_2} - \frac{2\cos\theta}{\sin}\left(\frac{\partial^2 U}{\partial\varphi_1\partial\psi} + \frac{\partial^2 U}{\partial\varphi_2\partial\psi}\right) + \frac{8\pi^2 A}{h^2}EU = 0 \qquad (9)$$

when the potential energy V is set equal to zero. Using the following substitution

$$\psi(\text{rotation}) = U = \Theta(\theta)\,e^{i(\lambda_1\varphi_1 + \lambda_2\varphi_2 + m\psi)} \qquad (10)$$

one obtains the differential equation for $\Theta(\theta)$

$$\frac{\partial^2\Theta}{\partial\theta^2} + \cot^*\frac{\partial\Theta}{\partial\theta} - \frac{(m - \lambda\cos\theta)^2}{\sin^2\theta}\Theta + \left[\frac{8\pi^2 A}{h^2}E - \frac{A}{C}(\lambda_1^2 + \lambda_2^2)\right]\Theta = 0 \qquad (11)$$

in which $A = \lambda_1 + \lambda_2$, and λ_1 and λ_2 are integers. This is the same **equation** that was obtained in the solution of the simple symmetrical top problem, and yields functions such as are given in equation *(5)*.

The solution of the problem may then be written

$$\psi\ \textbf{(rotation)} = \left\{ \begin{array}{l} v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right) e^{\pm i(\lambda_1\varphi_1 + \lambda_2\varphi_2 + m\psi)} \\ \\ v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right) e^{\pm i(\lambda_1\varphi_1 + \lambda_2\varphi_2 - m\psi)} \end{array} \right. \tag{12}$$

with $j \geq \lambda = \lambda_1 + \lambda_2 \geq 0$; $j \geq m \geq 0$. The meaning of the function $v_{j,m,\lambda}$ is given under equation (5). The equation for the energy is

$$E = \frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)\lambda^2 - \frac{2\lambda_1\lambda_2}{C}\right] \tag{13}$$

Although the equation is most easily solved in the coordinates φ_1 and φ_2 it would appear natural to transform to coördinates $\varphi = (\varphi_1 + \varphi_2)/2$ and $\varphi' = (\varphi_1 - \varphi_2)/2$, the "average" angle φ, and the angular displacement φ' of one CH_3 group from this average angle The displacement of the other group is of course equal to $-\varphi'$. In all higher approximations the potential energy will depend only on φ'. The equations then become

$$\psi\ \textbf{(rotation)} = \left\{ \begin{array}{l} v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right) e^{\pm i(\lambda\varphi + m\psi + \lambda'\varphi')} \\ \\ v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right) e^{\pm i(\lambda\varphi - m\psi + \lambda'\varphi')} \end{array} \right. \tag{14}$$

with $\lambda = \lambda_1 + \lambda_2$ and $\lambda' = \lambda_1 - \lambda_2$. The quantum numbers must obey the relations $j \geq \lambda \geq 0$; $j \geq m \geq 0$; $\lambda' = \lambda \pm 2n$, where n is an integer, that is, λ and λ' are both odd, or both even. The energy expressed in terms of the new quantum numbers becomes

$$E = \frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1) + \left(\frac{1}{2C} - \frac{1}{A}\right)\lambda^2 + \frac{(\lambda')^2}{2C}\right] \tag{15}$$

While this paper was being prepared for publication, there has appeared an article by Nielson[17] in which the ethane-like molecule is handled in a much more elaborate manner. His equations, when the potential energy of rotation within the molecule is set equal to zero, reduce to equation (14).

The entropy of a mole of such rotators may be calculated for high temperatures, in which case it becomes identical to the entropy of a mole of similar classical rotators with appropriate constants. The condition for the temperature is that $h^2/8\pi^2CkT$ and $h^2/8\pi^2AkT$ shall both be considerably smaller than 1. Actually values of about one fourth suffice for this condition. The equation for the entropy is

$$S_{\text{rotation}} = R\left[\ln 64\pi^5\left(\frac{kT}{h^2}\right)^2 AC + 2\right] \tag{16}$$

For ethane, could the two CH_3 groups not rotate separately around the C–C bond, the symmetry number would be 6; with free rotation, however, 18 permutations of the identical atoms can be carried out by changes in the angle coordinates. It is obvious further that the argument of the previous section applies as well to rotations of the angle φ' as to rotations

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[17] Nielson, *Phys. Rev.*, 40, 445 (1932).

of φ, and that the entropy will be reduced by subtraction of R In σ, with a = 18.

The Entropy Equations

Equations (1) or (4) give the entropy of a diatomic molecule of two unlike atoms at temperatures above about 200°K. but not high enough to produce any appreciable electronic excitation. Ordinarily one can safely use the equations up to 1000°K.

A diatomic molecule of two identical atoms will have the symmetry number a = 2 and to equation (1) or (4) must be added $-\text{R} \ln \text{a} = -\text{R} \ln 2$.

A linear polyatomic molecule will have an entropy given by an equation that differs from (1) or (4) only in that there will be more terms $S_{\text{Ein}}(\nu, T)$. In a triatomic linear molecule there are four vibrational degrees of freedom and four terms $S_{\text{Ein}}(\nu, \text{T})$, two of the frequencies usually the two lowest, those due to bending, will in most cases be identical. This means that spectroscopically only one (degenerate) frequency will be found, but two entropy terms must be used for this frequency. The symmetry number may be 1 or 2.

For non-linear rigid polyatomic molecules the entropy of rotation will be greater due to the greater number of degrees of freedom. There will also be at least three frequencies of vibration. In general if there are N atoms in the molecule, one must account for $3N-6$ vibrational degrees of freedom. Some observed frequencies may be degenerate, the assignment of the number of degrees of freedom to any frequency is a problem which may be solved by mathematical[18] or by mechanical[19] means.

The equation for the entropy of a rigid non-linear polyatomic molecule is

$$S = R\left[\ln \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{5/2}\left(\frac{8\pi^{7/3}(ABC)^{1/3}kT}{h^2}\right)^{3/2} e^{3/2}\, p_e p_n \cdot \frac{1}{\sigma} I + \sum_{i=1}^{i=3N-6} S_{\text{Ein}}(\nu_i, T)\right] \quad (17)$$

in which **I** is the number of physically distinguishable optical isomers, and with A, B and C the three moments of inertia. The explanation of the other symbols is given under equation (1). This may be written, at 1 atm. pressure

$$S = R\left[2.307 + 4 \ln T + 3/2 \ln \text{W} + 1/2 \ln A'B'C' + \ln p_e p_n I/\sigma + \sum_{i=1}^{i=3N-6} S_{\text{Ein}}(\nu_i, T)\right] \quad (18)$$

in which $A' = \text{A} \times 10^{38}$, $B' = B \times 10^{38}$ and $C' = C \times 10^{38}$.

If two of the moments of inertia A and B are equal the molecule is a

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[18] See for instance Mulliken, *Rev. Modern* Phys., 2, 60, 506 (1930); 3, 90 (1931).

[19] Kettering, Shutts and Andrews, *Phys. Rev.*. 36, 531 (1930).

symmetrical top and the equations (17) or (18) may still be used with this substitution.

A molecule of the ethane type will have 3N—7 vibrational degrees of freedom. The equation for the entropy may be written

$$S = R\left[\ln \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{5/2}\left(\frac{8\pi^{5/2}(AC)^{1/2}kT}{h^2}\right)^2 e^2\, p_e p_n \frac{1}{\sigma} I + \sum_{i=1}^{i=3N-7} S_{\mathrm{Ein}}(\nu_i, T)\right] \tag{19}$$

which reduces at 1 atm. pressure to

$$S = R\left[3.841 + 9/2 \ln T + 3/2 \ln W + \ln A'C' + \ln p_e p_n I/\sigma + \sum_{i=1}^{i=3N-7} S_{\mathrm{Ein}}(\nu_i, T)\right] \tag{20}$$

with $A' = A \times 10^{38}$, $C' = C \times 10^{38}$.

Accuracy

The accuracy with which the universal physical constants that enter the entropy equations are known is undoubtedly far greater than any practical use of the entropy demands. The molecular weight also introduces no error. The uncertainty in the use of these equations lies partly in the assumptions of their derivation and partly in the accuracy with which the moments of inertia and the frequencies are known.

The assumption that the moments of inertia in all states existing in appreciable quantities remain constant can be roughly tested by calculation of the stretching force constant from the frequencies. In most cases the average change in the moment of inertia up to 1000°K. is less than 8%, introducing about 0.1 Entropy Unit (cal. deg.^{-1}) error per rotational degree of freedom at this temperature. Failure of the vibrations to be linear harmonic probably introduces even less error. The assumption that ethane-like molecules rotate freely about the C–C bond is much more questionable. Ebert[20] and Wagner[21] have discussed the question of how "free" the rotation really is in ethane, basing their discussion largely on the specific heat measurements of Heuse[22] which were carried out in 1913–1914. The specific heat values appear to agree with those of a fully excited vibrator, rather than with the lower specific heat of a free rotator; it may be questioned, however, whether data of that date are sufficiently accurate to decide the question.

Although the calculations, if carried out for the constrained rotating oscillator, would use a = 6 and correspondingly three times as many isomer functions as here used, the phase space would be constrained to one-third of the total angle 2π, instead of the full rotational angle, and the

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[20] Ebert, "Leipziger Vortrage," 1929, p. 74.

[21] *Carl Wagner, Z. physik. Chem., [B] 14,* 166 (1931).

[22] Heuse, *Ann. Physik, 59,* 86 (1919).

entropy based on such an assumption would approach, with decreasing potential energy, that of the free rotator of equation (20). We believe that for ethane itself, at least, the entropy will be given fairly well by equation (20). More accurate measurements of the specific heat and entropy appear to be the only experimental method of decision.

The moments of inertia of some molecules can be obtained from spectroscopic data. Usually no values so obtained are available, but the spacing of the atoms can frequently be accurately estimated from x-ray data for the molecule in question or for some similar compound. With the usual assumptions for the geometrical structure these data probably allow calculations of the moments of inertia for the simpler organic compounds to within at least 10%, introducing 0.1 Entropy Unit error per rotational degree of freedom. The total entropy of one vibrational degree of freedom with frequency 200 cm.^{-1} at 300°K. is 2.16 E. U., and for 1100 cm.^{-1} at 300°K. it is only 0.03 E. U. An error of 10% in the value of the frequency introduces an error of 0.2 E. U. in the first case and no appreciable error in the second. Much more important is the correct assignment to each frequency of the number of degrees of freedom, and the certainty with which one can assume that all frequencies are known. Much progress has been made in the interpretation of the lower, and less numerous, frequencies[19] which are due to the mutual vibrations of the heavier atoms. In many cases one can feel quite confident that the interpretation is correct. Fortunately the less certain frequencies due to the motion of the hydrogen atoms appear to be all above 1100 cm.^{-1} and introduce less than 0.03 E. U. at 300°K. per degree of freedom

It appears not unreasonable to expect that we can calculate the entropies of many of the simpler organic compounds to within 0.5 cal. deg.^{-1}. This would introduce barely 30% error in an equilibrium constant prediction.

The Entropy of Some Simple Molecules

Ethane.—The moment of inertia C of the CH_3 group about the C–C bond will be equal to the moment of inertia of methane, if the tetrahedral angle for the hydrogen bonds is approximately maintained in ethane. The moment of inertia of methane is known from its band spectra.[23] x-Ray data show that the C–C distance in aliphatic hydrocarbons has a constant value, and this with the C–H distance calculated from the moment of inertia of methane gives the other moment A of the ethane molecule

The Raman line at 990 cm.^{-1} is undoubtedly due to the mutual vibration of the two methyl groups, and will have one degree of freedom. The assignment of the other frequencies, 4 at 1200 cm.^{-1} and 6 at 1460 cm.^{-1} both due to hydrogen "bending" is pure guess, especially since no line at 1200 is observed, but the total entropy which these contribute is so low (0.2 E. U.) that the assignment is unimportant.

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[23] Moorhead, *Phys. Rev.*, 39, 83 (1932).

The following constants are then used for ethane in equation (20) to calculate the entropy at 1 atm. pressure, 298°K.: W = 30; C' = moment of inertia of methane, $C \times 10^{38} = 0.0517$; A', calculated from C–C distance 1.55 Å. and C–H distance 1.08 Å., is 0.417; $h = 2^6 = 64$; $p_e = 1$; $\sigma = 18$; ν_1, 1 degree of freedom 990 cm.$^{-1}$; ν_2, 4 degrees of freedom 1200 cm.$^{-1}$; ν_3, 6 degrees of freedom 1460 cm.$^{-1}$; total vibrational entropy at 298°K. = 0.26 E. U. For ethane gas, 298°K., 1 atm., the total absolute molar entropy $S = 63.8$ cal. deg.$^{-1}$, of which R ln 64 = 8.3 due to nuclear spin may be neglected, leaving for the practical entropy $S_p = 55.5$.

Acetylene.—A band in the infra-red spectrum of acetylene[24] at 730 cm.$^{-1}$ may possibly contribute 4 degrees of freedom and 0.5 E. U. at 298°K. It seems more probable that this band is not a fundamental and that the lowest fundamental, contributing 4 degrees of freedom due to hydrogen "bending," is at 1330 cm.$^{-1}$. The following entropy may be as much as 0.5 E. U. too low because of this assumption The constants used in equation (4) with 4 of the total 7 frequencies contributing an appreciable entropy are: W = 26; $A' = 0.23$;[25] $p_e = 1$; $p_n = 2^2 = 4$; a = 2; ν_1, 4 degrees of freedom, 1330 cm.$^{-1}$ contributing 0.1 E. U. at 298°K. For acetylene gas, 1 atm., 298°K. the total absolute entropy, $S = 49.9$ cal. deg.$^{-1}$, of which 2.7 E. U. are due to nuclear spin, leaving a practical entropy $S_p = 47.2$ E. U.

Benzene.—Andrews[19] has obtained excellent agreement between the Raman lines of benzene and his models, which enables us to assign the number of degrees of freedom to the frequencies with considerable certainty. x-Ray data on hexamethylbenzene and graphite,[26] and electron diffraction data on gaseous benzene,[27] allow us to estimate the C–C distance accurately. The C–H distance, which is unimportant in the moments of inertia, is assumed to be that of methane. The following constants are substituted in equation (18): W = 78; $A' = B'$, calculated from C–C = 1.42 Å. and C–H = 1.08 Å., is 1.508; $C' = 3.016$; $p_e = 1$; $p_n = 64$; $\sigma = 6$

ν_1, 2 degrees of freedom = 360 cm.$^{-1}$
ν_2, 1 degree of freedom = 605 cm.$^{-1}$
ν_3, 2 degrees of freedom = 805 cm.$^{-1}$
ν_4, 6 degrees of freedom = 990 cm.$^{-1}$
ν_5, 1 degree of freedom = 1170 cm.$^{-1}$
ν_6, 12 degrees of freedom = 1590 cm.$^{-1}$

other frequencies too high to contribute to the entropy. The total vibrational entropy at 298°K. is 3.8 E. U. For benzene gas, 1 atm., 298°K., the total absolute entropy $S = 73.4$ cal. deg.$^{-1}$, of which R ln 64 = 8.3

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[24] Levin and Meyer, J. Opt. *Soc.* Am., 16, 137 (1928).

[25] From infra-red measurements.[24]

[26] Ewald and Hermann, "Strukturbericht," 1913–1928.

[27] Wierl, Ann. *Physik*, 8, 521 (1931).

E. U. are due to nuclear spin, leaving a practical entropy, S_p = 65.1 cal. deg.$^{-1}$.

The experimental entropy of the liquid at 298°K. is 41.9 E. U. and the entropy[28] of vaporization at the equilibrium vapor pressure at this temperature, 94 mm., is 27.5 E. U. To the sum of these must be added −4.3 E. U. to convert to 1 atm., making the experimental entropy of benzene gas at 1 atm., 298°K., 65.1 E. U.

The value of a = 6 for benzene was calculated by Deitz[29] from measurements of the vapor pressure. The less structure sensitive methods of x-ray and electron diffraction have hitherto always indicated plane structure for the carbon atoms, which would lead one to assume a = 12. An undetected transition in the solid state of benzene below the lowest temperatures of the specific heat determinations could only lead to a lower value of a. The excellent constancy of the a as calculated by Mr. Deitz over a wide range of temperatures (from 100°K. to 298°K. a varied from 5.4 to 6.9) indicates, we believe, conclusively, that all twelve atoms of benzene do not lie in one plane.

Summary

It has been shown that any molecule will have among the additive terms in the entropy expression: $-R$ ln a, with a the symmetry number; R $\ln(2s_i + 1)$ for every atom i of spin s_i; R ln I, with I the number of distinguishable optical isomers present in the gas.

The quantum mechanical wave functions and the energy values of an ethane-like molecule have been calculated under the assumption of free independent rotation of the two CH_3 groups about the C–C bond. The entropy of this type of molecule has also been calculated.

Convenient expressions have been given for the molal entropy of diatomic, rigid linear and non-linear polyatomic, and ethane-like molecules.

The data necessary for the entropy evaluations have been reviewed, and the accuracy which can be expected has been briefly discussed. It appears probable that for many of the simpler organic gases the entropy can be calculated with present data to within 0.5 E. U. (cal deg.$^{-1}$).

The practical molar entropies (neglecting nuclear spin which cancels in all chemical reactions), of ethane, acetylene and benzene gases at 1 atm., 298°K., have been calculated to be 55.5, 47.2 and 65.1 E. U., respectively.

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[28] Parks and Huffman, THIS JOURNAL, 52, 1032 (1930).

[29] Victor Deitz, *J. Chem. Physics*, 1, January, 1933.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Line Spectrum of Samarium Ion in Crystals and its Variation with the Temperature

BY SIMON FREED AND J. G. HARWELL

The magnetic behavior of Sm^{+++}[1] and the absorption spectra[2] showed that there was an equilibrium distribution of the ions between different electronic configurations. The present work was instituted with the view of obtaining quantitative data concerning the differences in energy between the various configurations. These differences may be looked upon as originating through the action of the electric fields about Sm^{+++} in the lattice. They are a measure of their symmetry and intensity. Recently, Miss Amelia Frank[3] obtained rough agreement with the magnetic susceptibility at higher temperatures by taking into account the presence of the activated state $^6H_{7/2}$, presumably about 1000 cm.$^{-1}$ higher in energy than the basic state $^6H_{5/2}$. The agreement is rather surprising since both the basic state, $^6H_{5/2}$ and active state, $^6H_{7/2}$ are largely decomposed into sublevels of wide separation by the electric fields of the lattice. The specific heat of Sm^{+++}[4] at low temperature has given a measure of the separations between the basic electronic levels. It appeared that energy of about 160 cm.$^{-1}$ (450 cal./mole) had to be supplied to activate a mole of Sm^{+++} in the sulfate. Even greater intervals may have resulted in the decomposition of the $^6H_{5/2}$ term, but they must be so great that relatively few ions exist in the upper level.

The present work is mainly concerned with the effect of the electric fields upon the state $^6H_{5/2}$, that is, with levels which are sufficiently occupied at ordinary temperatures to have their presence recorded in the absorption spectrum. They are identified by the change in the relative intensity of the lines as the temperature changes, more especially by those instances when a line increases in intensity apparently at the expense of a neighboring line. When this line is of higher frequency than the one whose intensity is decreasing, there is considerable probability that the lines arise at two levels slightly different in energy and end in a common energy level. And the recurrence of the same interval in different regions of the spectrum practically establishes the existence and separation of the lower energy levels.

The experimental method has been described[6] in another connection. A hydrogen discharge tube served as the source of the continuous radiation

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[1] Freed. THIS JOURNAL, 52, 2702 (1930).

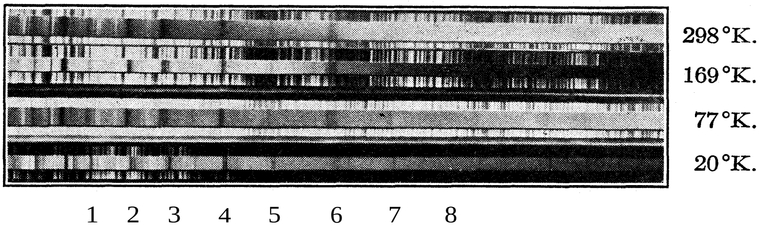
Freed and Spedding, Nature, 123, 525 (1929).

[3] Amelia Frank, Phys. Rev., 39, 119 (1932).

[4] Ahlberg and Freed, *ibid.*, 39, 540 (1932).

[5] Freed, *ibid.*, 38, 2122 (1931).

and the spectra extended from 4200 to about 2200 Å. A Hilger spectrograph of the type E2 was employed. The radiation was passed parallel to the optic axis of the hexagonal crystal[6] $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ which was about 0.5 mm. thick. For the purpose of lowering the temperature of the crystal, liquid hydrogen (20°K.), liquid nitrogen (77°K.), and liquid ethylene (169°K.) were used, all boiling at atmospheric pressure. The average absolute error in the measurement of the lines is about 5 cm.$^{-1}$. Some of the lines were faint or diffuse and there has been listed next to each line in the table the number of times it was measured and the reproducibility of the measurement. The recorded intensities are visual estimates and should be trusted only as a measure of relative intensity within a restricted region of the spectrum and in spectra originating at the same temperature.



Absorption spectrum of Sm^{+++} in $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$.

The group of lines assigned to energy levels have undergone such changes in intensity that the increase or decrease in intensity of one line with respect to another could be told at a glance on an enlargement of the spectrogram.

ABSORPTION LINES OBTAINED AT 20°K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
2 D	42,940 ± ?	1	2 D	28,241 ± 1	2
2 D	42,915 ± 1	2	1 S	28,184 ± ?	1
3 S	42,867 ± 2	4	3 D	28,149 ± 0	2
3 B	42,834 ± 1	4	2 D	28,138 ± 3.5	2
5 S	42,542 ± 3	3	7 D	27,639 ± 1	2
5 S	42,513 ± 3	3	10 B	27,629 ± 1	2
5 B	42,457 ± 1	4	7 B	27,597 ± 0	2
5 B	42,321 ± 1	4	5 B	27,585 ± 3.5	2
1 S	42,260 ± 2	4	5 B	27,537 ± 0	2
2 S	42,025 ± 1	4	2 D	27,469 ± 1	2
Faint	42,002 ± ?	1	Faint	27,403 ± ?	1
3 B	41,949 ± 1	4	Faint	26,934 ± ?	1
Faint	38,381 ± ?	1	Faint	26,885 ± ?	1
2 S	37,508 ± 1	2	3 D	26,735 ± 2	3
Paint	37,486 ± ?	1	1 S	26,708 ± ?	1
2 S	37,474 ± 2	2	5 B	26,670 ± 1.5	4

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[6] Jaeger, *Rec. trav. chim.*, 33,362 (1914).

ABSORPTION LINES OBTAINED AT 20°K. *(Concluded)*

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	36,540 ± ?	1	4 B	26,650 ± 0	2
Faint	36,523 ± ?	1	4 S	26,621 ± 0	2
3 S	35,857 ± 1	2	10 B	26,597 ± 2	2
3 B	35,834 ± 2	4	Faint	26,566 ± ?	1
3 D	34,464 ± 6	4	Faint	26,514 ± ?	1
Faint	33,800 ± ?	1	Faint	26.487 ± ?	1
2 S	33,656 ± 1	2	Faint	26,449 ± ?	1
2 D	33,641 ± 1	2	Faint	26,408 ± ?	1
Faint	33,569 ± 1	2	Faint	26,372 ± ?	1
Faint	33,515 ± ?	1	2 D	26,296 ± ?	1
Faint	33,490 ± 2	2	2 S	26,261 ± ?	1
1 S	33,103 ± ?	1	2 S	26,230 ± ?	1
1 S	33,074 ± ?	1	2 S	25,943 ± ?	1
3 S	32,721 ± 0	2	2 S	25,915 ± ?	1
4 B	32,708 ± 1	2	2 S	25,793 ± ?	1
2 S	32,691 ± 1	2	2 S	25,775 ± 1	2
Faint	32,632 ± ?	1	2 S	25,739 ± 4	3
3 D	31,530 ± 1	2	2 S	25,714 ± ?	1
2 B	31,511 ± 1	2	Faint	25,614 ± ?	1
5 S	31,463 ± 0	2	5 B	25,586 ± 3	4
4 B	31,448 ± ?	1	5 B	25,543 ± 1.5	2
2 D	31,401 ± 1	3	5 S	25,536 ± 2	2
1 D	31,353 ± 4	4	1 S	25,485 ± 5	2
Faint	30,218 * ?	1	2 D	25,186 ± 0	2
2 S	30,211 ± 1 5	2	1 S	25,151 ± ?	1
2 S	30,133 ± ?	1	4 D	25,107 ± 0	2
3 D	30,115 ± 1.5	2	2 S	25,083 + 3	2
Faint	30,106 ± 1.5	2	1 S	24,987 ± ?	1
1 D	30,071 ± 1.5	2	1 S	24,965 ± ?	1
2 D	30,058 ± 1	2	10 B	24,919 ± 0	3
Faint	29,970 ± 0	2	10 B	24,869 ± 4	4
2 S	29,953 ± 2 5	2	1 S	24,730 ± 4	3
Faint	30,000 ± ?	1	1 S	24,681 ± ?	1
1 D	29,937 ± ?	1	1 S	24,669 ± 1.5	2
1 D	29,255 ± 0.50	2	5 B	24,522 ± 1	2
1 D	29,173 ± 0	2	1 S	24,487 ± ?	1
Faint	29,084 ± ?	1	1 S	24,466 ± 3	2
5 B	29,008 ± 0	2	1 S	24,451 ± ?	1
7 S	28,996 ± 3	2	3 D	24,417 ± 4	3
4 S	28,964 ± 1.5	2	2 S	24,376 ± 2	3
4 D	28,949 ± 1	2	2 D	24,334 ± 2	2
5 S	28,936 + 1	2	1 S	24,082 ± 5	2
5 D	28,924 ± 1	2	1 S	24,054 ± ?	1
Faint	28,251 ± 2	2	7 S	24,016 ± 0	4

ABSORPTION LINES OBTAINED AT 77°K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	42,862 ± 1	2	3 D	30,121 ± 2	2
3 B	42,834 ± 1	4	1 B	30,067 ± 1	4
2 S	42,538 ± 1	2	5 B	29,010 ± 2	4

ABSORPTION LINES OBTAINED AT 77°K. *(Concluded)*

Intensity	Wave number	Measured	Intensity	Wave number	Measured
2 S	42,513 ± ?	1	5 S	28,996 ± ?	1
3 B	42,457 ± 3	4	Faint	28,978 ± ?	1
3 B	42,430 ± 1	2	5 B	28,945 ± 3	4
3 D	42,423 ± 1	2	3 S	28,936 ± ?	1
2 S	42,374 ± ?	1	Faint	28,251 ± ?	1
2 S	42,351 ± ?	1	5 B	27,647 ± 1	4
3 B	42,319 ± 1	4	2 D	27,595 ± 2	4
2 S	42,283 ± ?	1	5 B	27,540 ± 1	4
2 B	42,251 ± 1	4	5 B	27,478 ± 1	4
Faint	42,023 ± 2	2	1 S	26,737 ± I	3
1 S	41,976 ± ?	1	1 S	26,708 ± 1	4
3 B	41,949 ± 1	4	5 S	26,664 ± 2	3
1 S	37,579 ± ?	1	5 S	26,643 ± 2	3
1 S	37,564 ± ?	1	5 S	26,623 ± 2	3
1 S	37,536 ± 3	2	10 B	26,604 ± 1	3
1 S	37,508 ± 4	2	5 S	26,581 ± 1	2
1 S	37,481 ± ?	1	Faint	26,432 ± ?	1
2 D	37,450 ± 1	4	Faint	26,378 ± ?	1
Faint	37,404 ± ?	1	1 S	26,257 ± 0	2
Faint	37,306 ± ?	1	Faint	25,976 ± 2	2
Faint	37,287 ± ?	1	Faint	25,931 ± 1	2
Faint	37,275 ± ?	1	1 S	25,786 ± 1	2
1 S	37,000 ± 1	2	1 S	25,746 ± 1	2
2 D	35,846 ± 2	4	1 S	25,664 ± ?	1
2 D	35,833 ± 0	2	2 S	25,588 ± 2 5	4
2 D	35,777 ± 3	4	I S	25,544 ± ?	1
Faint	34,714 ± ?	1	2 S	25,532 ± 1	3
Faint	34,628 ± ?	1	1 S	25,503 ± 1	2
2 D	34,467 ± 2	4	2 D	25,186 ± 5	3
1 S	34,415 ± 0	2	1 S	25,153 ± 0	3
1 S	34,409 ± 1	3	2 D	25,108 ± 2	3
1 S	34,384 ± ?	1	2 B	25,077 ± 0	2
1 S	34,370 ± ?	1	1 S	25,008 ± 2	2
1 S	34,351 ± 2	4	1 S	24,981 ± 3	3
3 B	32,723 ± I	4	I S	24,959 ± ?	1
1 S	32,686 ± 2	4	1 S	24,935 ± 0	2
2 D	32,655 ± 2	4	1 S	24,910 ± 2	3
2 D	31,533 ± 1	2	10 B	24,888 + 2	2
3 D	31,511 ± ?	1	10 B	24,794 ± 1	4
2 D	31,502 ± 1	3	2 S	24,725 ± ?	1
3 D	31,497 + ?	1	5 B	24,532 ± 1	2
3 D	31,461 ± 1	4	5 B	24,493 ± 1	2
2 D	31,408 + 2	4	2 S	24,136 + ?	1
3 D	31,364 ± 1	4	Faint	24,047 ± ?	1
			7 S	24,016 ± 0	4

ABSORPTION LINES OBTAINED AT 169°K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	37,514 ± ?	1	5 B	27,549 ± 0	2
2 D	37,457 ± 1	2	5 B	27,491 ± 0	2

ABSORPTION LINES OBTAINED AT 160°K. *(Concluded)*

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	35,838 ± 0	2	1 S	27,439 ± ?	1
Faint	35,777 ± 0	2	1 S	27,405 * ?	1
Faint	34,680 * ?	1	1 S	27,349 ± ?	1
Faint	34,533 * ?	1	1 S	27,307 ± ?	1
Faint	34,467 * 1	2	Faint	26,850 ± ?	1
Faint	34,418 ± 0	2	Faint	26,800 ± ?	1
Faint	34,360 ± 1	2	1 S	26,762 ± ?	1
3 D	32,728 ± 1	2	1 S	26,736 ± 0	2
3 D	32,666 ± 1	2	5 S	26,654 ± 1.5	2
1 D	31,903 ± ?	1	5 B	26,609 ± 2.5	2
1 D	31,883 ± ?	1	2 S	25,596 ± 2	2
Faint	31,540 ± ?	1	1 D	25,550 ± 0	2
3 B	31,510 ± ?	1	1 S	25,200 ± 0	2
Faint	31,505 ± ?	1	1 D	25,119 ± 1.5	2
Faint	31,494 ± ?	1	1 S	24,936 ± 1	2
2 D	31,458 ± 1.5	2	1 S	24,919 ± 2	2
2 D	31,416 ± 1	2	10 B	24,895 ± 2	2
3 D	31,371 ± 1	2	10 B	24,814 ± 0	2
2 D	31,295 ± ?	1	1 S	24,742 ± ?	1
1 D	31,259 * ?	1	1 S	24,669 ± 1	2
1 S	30,169 ± ?	1	1 S	24,627 ± 3	2
Faint	30,158 * ?	1	3 D	24,567 ± ?	1
1 S	30,118 ± 1	2	5 B	24.529 ± 3	2
2 D	30,072 ± 2	2	5 B	24,511 ± ?	1
5 B	29,015 ± 2.5	2	1 S	24,535 ± 1	2
7 B	28,955 ± 0	2	1 S	24,350 ± 0	2
1 S	28,673 ± ?	1	5 S	24,037 ± 1	2
1 S	28,642 ± ?	1	3 S	23,986 ± 1.5	2
5 B	27,639 ± 0	2	3 D	23,941 ± 1	2
1 S	27.591 ± 1	2			

For convenience, the groups have been numbered on the reproductions of the spectra. Below each diagram is given a list of the frequencies derived from the energy levels and these are compared with the observed frequencies for each group of lines. All the deviations are well within the errors of measurement. Groups 4, 7, 8 and 10 under low dispersion appear as doublets having the same energy difference at each temperature. Under higher dispersion, each line is found to be doubled and with the data in hand it is impossible to prove rigorously whether the "fine-structure" energy level belongs to the basic term system or not. More data, we are informed, will be available soon in a more extensive paper by Spedding and Bear from Berkeley? If the "fine-structure" level is assigned to the basic multiplet, it becomes possible to include the quartet 5 and also the sextet: *3* and 6. This arrangement of levels has a considerable degree of probability and by its aid all the multiplets in which marked intensity changes occur can be interrelated.

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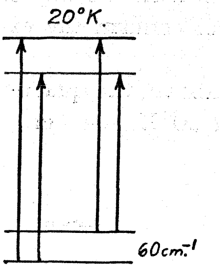
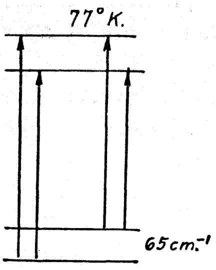
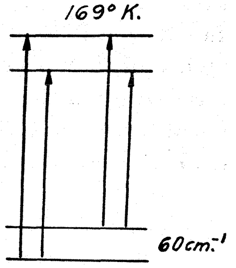
[7] Spedding and Bear, *Phys. Rev.*, in press.

Below is a typical example of an energy level pattern which the quartets 4, 7, 8 and 10 accord with and also the basic separations which are valid for all of them. The intensities too agree with these assignments.







Group	Temp., °K.	Separation of upper level, cm.⁻¹	Calcd. line, cm.⁻¹	Observed line, cm.⁻¹	Deviation. cm.⁻¹
4	20	12		29,008 **(accepted)**	
			28,996	28,996 ± 3	0
			28,948	28,949 ± 1	1
			28,936	28,936 ± 1	0
	77	12		29,010 **(accepted)**	
			28,998	28,996 ± ?	2
			28,945	28,945 ± 3	0
			28,933	28,936 ± ?	3
	169			29,016 **(accepted)**	
			28,956	28,955 ± 0	1
7	20	12		32,721 **(accepted)**	
			32,708 **too faint**		
	77			32,723 ± 1 **(accepted)**	
			32,658	32,655 ± 2	3
	169			32,728 ± 1 **(accepted)**	
			32,668	32,666 ± 1	2
8	20	23		35,857 **(accepted)**	
			35,834	35,834	
	77	12		35,846 ± 2 **(accepted)**	
			35,834	35,833 ± 0	1
			35,781	35,777 ± 3	4
	169			35,838 ± 0	
			35,778	35,777 ± 0	1
10	20			42,321 ± **(accepted)**	
			42,261	42,260 ± 2	1
	77			42,319 ± 1 **(accepted)**	
			42.254	42,251 ± 1	3

Some of the lines which one would normally expect from these levels were too faint to be measured. At higher temperatures, some of the lines were so diffuse that the average between two unresolved lines is given.

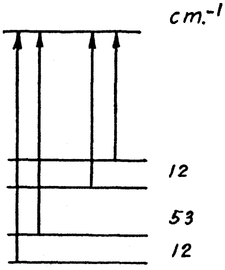
There can be no doubt concerning the existence of an interval of 60 cm.$^{-1}$ (at 20°K., 65 cm.$^{-1}$ at 77°K. and 60 cm.$^{-1}$ at 169°K.) between two energy levels in the basic multiplet. Also, there is little doubt but that this interval can be related to the influence of the electric fields of the lattice upon $^6H_{5/2}$. It may be predicted at this point that a close study of the specific heat measurements at low temperatures will confirm the existence of this interval.

Based upon the same pattern of levels as those given above, the quartet 5 will have the following basic intervals: 60 cm.$^{-1}$ at 20°K., 54 cm.$^{-1}$ at 77°K. and 43 cm.$^{-1}$ at 169°K.

Group	Temp., °K.	Calcd. line, cm.$^{-1}$	Obs. line, cm.$^{-1}$	Deviation
5	20		30,115 ± 2 *(accepted)*	
		30,130	30,133 ± ?	3
		30,070	30,071 ± 2	1
		30,055	30,058 ± 1	3
	77		30,121 ± 2 *(accepted)*	0
		30,007	30,067 ± 1	
	169		30,118 ± 1	
		30,075	30,072 ± 2	3

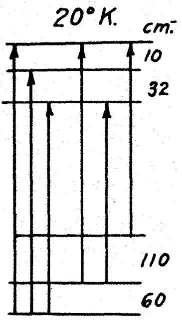
Now it is clear that if the 12 cm.$^{-1}$ interval (the "fine-structure" interval) is inserted in the basic multiplet of *4*, 7, *8*, 10, the group 5 fits into the same scheme as groups *4*, *7*, *8*, *10* and we shall see later the sextets *3* and 6 will also be associated with the same levels. As an example we shall give the energy levels of group *4* and *5* at 77°K., employing the same basic multiplet for both.

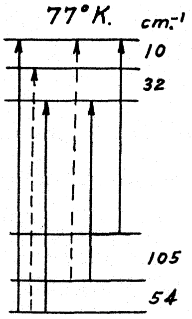
Quartets 4 and 5
77° K.

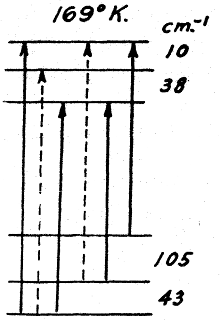


The fact that the "fine structure" interval is of the same magnitude in all groups (with the possible exception of *8*) is evidence for including it in the basic multiplet. Its inclusion results naturally in any attempt to superpose the levels of the groups for the purpose of obtaining all the components into which $^6H_{5/2}$ has been split. It must be stated again that more data are necessary for this purpose, especially spectra at the temperature of liquid helium.

Since the spectrum of Sm^{+++} consists of rather isolated groups, one would expect the lines to originate and end at neighboring levels. The intensities justify this point of view as the components of greater frequency always become more intense as the temperature is reduced. The sextets *3* and 6 contain the same energy interval as the quartet *5* and the intensities of corresponding lines behave in the same way with regard to temperature. We shall therefore associate *3* and 6 with the same basic states as 5. Below is the energy level pattern of *3* based upon that of 5.







Temp., °K.	Calcd. line, cm.$^{-1}$	Obs. line, cm.$^{-1}$	Deviation, cm.$^{-1}$
20		27,639 ± 1 (accepted)	
	27,629	27,629 ± 1	0
	27,597	27,597 ± 0	0
	27,579	27,585 ± 6	6
	27,537	27,537 ± 0	0
	27,469	27,469 ± 1	0
77		27,637 ± 1 (accepted)	
	27,595	27,595 ± 2	0
	27,543	27,540 ± 1	1
	27,478	27,478 ± 1	0
169		27,639 ± 0	
	27,591	27,591 ± 1	0
	27,548	27,549 ± 0	0
	27,491	27,491 ± 0	0

The sextet 6 follows a similar pattern, its first interval being identical at each temperature with that of *3* but the over-all separation of the basic multiplet is slightly different. This difference can probably be ascribed to another "fine structure" interval in the basic term system.

The lines which have been studied here because of the variation in their intensities constitute about one-half the prominent lines of the spectrum.

A part of this experimental work was done by one of us (S. F.) during his stay in the laboratory of Professor de Haas, Leyden, Holland, while he was a fellow of the John Simon Guggenheim Memorial Foundation.

Summary

The absorption spectra of Sm^{+++} in the hexagonal crystal $Sm(C_2H_5SO_4)_3\cdot 9H_2O$ were taken parallel to the optic axis at 20, 77 and 169°K. Absorption lines are listed in the region of the spectrum between 4200 Å. and 2200 A.

This paper is principally concerned with the various electronic configurations in the basic multiplet, especially as they result from the interaction of Sm^{+++} and the electric fields of the lattice. In consequence, all the lines whose relative intensities vary with the temperature have been studied in terms of energy level diagrams.

CHICAGO, ILLINOIS
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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Photodissociation of Hydrogen Peroxide in the Presence of Hydrogen and Carbon Monoxide and the Recombination of OH Radicals

BY GUENTHER VON ELBE[1]

The ultraviolet absorption spectrum of hydrogen peroxide in the gas phase has been determined by Urey, Dawsey and Rice.[2] The authors conclude that for every absorbed light quantum two hydroxyl radicals are formed according to the equation

$$H_2O_2 + h\nu = 2OH \qquad (1)$$

Hydroxyl radicals are also involved in Bonhoeffer and Haber's scheme of the hydrogen and carbon monoxide combustion[a]

$$H + O_2 + H_2 = H_2O + OH \qquad (2)$$

$$OH + H_2 = H_2O + H \qquad (3)$$

$$\text{or } OH + CO = CO_2 + H, \qquad (4)$$

This scheme has been discussed by Frankenburger and Klinkhardt[4] who carried out experiments on the action of photochemically generated hydrogen atoms in hydrogen and oxygen mixtures. They propose that reaction (2) should be followed either by (3) or by

$$OH + OH + M = H_2O_2 + M \qquad (5)$$

and that reaction (3) should require an activation energy of not less than 14,000 cal. An activation energy of that order would keep the rate of (3) sufficiently small until about 400° to make (5) the predominant reaction. The formation of chains would thus be prevented until about that temperature, which is consistent with the observed behavior of hydrogen–oxygen mixtures.

In the present work, mixtures of hydrogen peroxide vapor with hydrogen or carbon monoxide were exposed to the light of a condensed zinc spark. A small but distinct reaction was observed in both cases, suggesting the occurrence of reaction (1) and (3) or (1) and (4). In view of Frankenburger and Klinkhardt's work, most of these experiments were made with hydrogen. If OH was formed, according to (1), these experiments should allow one to test the reaction scheme proposed by these authors. In the

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(1) Research Associate, University of Virginia.

(2) Urey, Dawsey and Rice, THIS JOURNAL, 61, 1371 (1929).

(3) Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 263 (1928).

(4) Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **123**, 431 (1931); *Z. physik. Chem*, **15B**, 421 (1932).

first place, the observed rates of hydrogen consumption should correspond to an activation energy of not less than 14,000 cal. This is indeed the case,[5] but this fact alone is not sufficient for the test. The purpose may be achieved by varying the experimental conditions which influence the rate of hydrogen consumption. If the reaction scheme is right, one should be able to predict changes of this rate. If the observed changes do not check with those theoretically predicted within a reasonable limit, the scheme certainly would appear rather doubtful.

Experiments and Results

The apparatus consisted of a closed flow system filled with either hydrogen or carbon monoxide. The details will appear from the figure. The small bubbler within the thermostat contained a 95% hydrogen peroxide solution which was prepared as in the method of Rice, Reiff and Kilpatrick.[6] The liquid was sufficiently shielded against direct or stray radiation from the zinc spark. Oxygen within the system could be removed by passing the gas flow through a pyrogallol solution.

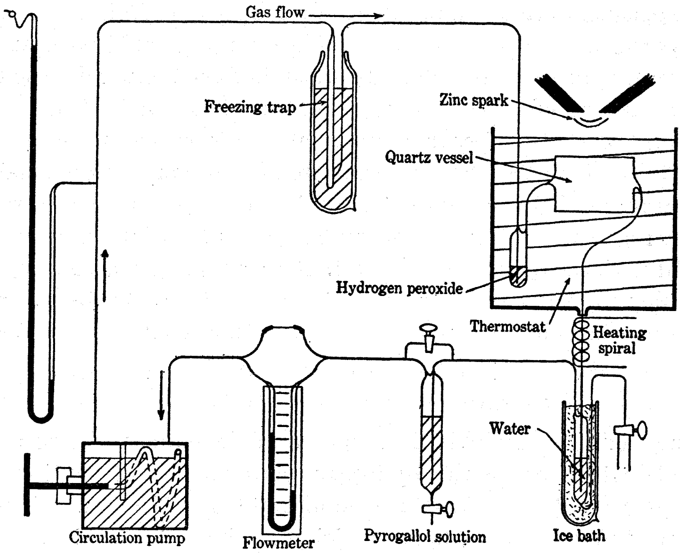

Fig. 1.—Apparatus for measuring photochemical reactions of hydrogen peroxide in the gas phase.

The data obtained are given in Table I. The first column shows the time for which the mixtures were exposed to ultraviolet light. The next three columns give the actual pressure changes effected by illumination. In some experiments, the oxygen was allowed to accumulate and afterward removed by pyrogallol. The fifth column contains the partial pressure of hydrogen peroxide in the mixture. It is calculated from the amount of hydrogen peroxide evaporated and the volume of hydrogen passing in a

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(5) Von Elbe and Lewis, THIS JOURNAL, 64, 652 (1932).

(6) Rice, Reiff and Kilpatrick, *ibid.*, 48,3019 (1926).

given time. The latter is given in the next column. The hydrogen peroxide was caught in a water trap, except for the small amount which was used in the reaction. This amount was so small, indeed, that it did not appreciably change the hydrogen peroxide partial pressure. At the end of the run the contents of the ice water trap were removed and titrated with 0.1 *N* potassium permanganate. The seventh column shows the temperature of the thermostat. The last two columns show the number of hydrogen molecules disappearing and oxygen molecules formed during the illumination per sec. per cc. Since the reaction took place in the quartz vessel only, these last values were obtained by dividing the total number of molecules disappearing or formed per second by the volume of the quartz vessel which was 86 cc. The total amount of hydrogen and oxygen disappearing per sec. was obtained from the observed rate of pressure change, as given by the first four columns, the temperature and the total volume of the apparatus, namely, 218 cc.

The experiments can roughly be divided into two groups: those at 40° and a hydrogen peroxide pressure of 4 to 5 mm., and those at 28° and about 2 mm. hydrogen peroxide. It was not advisable to raise the temperature much above 40°, because the decomposition of hydrogen peroxide in the liquid phase then became appreciable. It was also not advisable to go lower than about 28°, because the rate of reaction was too small.

The number of light quanta entering the vessel per sec. was estimated in the following way. Mixtures of hydrogen and hydrogen bromide were passed through the quartz vessel, while the zinc spark was running, and the free bromine formed was measured. According to E. Warburg, for each hv absorbed one bromine is formed.[7] The results are shown as follows

H Br partial pressure (mm. Hg)	52	98	118
$h\nu$ absorbed per sec. $\times 10^{-16}$	4.4	4.7	5.2

For the hydrogen bromide decomposition the same two line groups are responsible which cause the hydrogen peroxide decomposition, namely, the groups around 2070 Å. and around 2530 Å. However, they are absorbed at different percentages which can be calculated for hydrogen bromide from Warburg's data, and for hydrogen peroxide vapor from the work of Urey, Dawsey and Rice,[2] the length of the light path being, in the present case, 5 cm. In the above table, the apparent depending of the number of *hv* absorbed upon the hydrogen peroxide pressure may be attributed to changing absorption in the 2530 group. A calculation on this basis shows that the number of light quanta entering the vessel per sec. is 3.2×10^{16} in the 2070 group, and 2.4×10^{16} in the 2530 group. If the vessel is filled with hydrogen peroxide vapor at 5 mm., the first group will be absorbed to 26%, the other to 7%. The total absorption will amount to 1.0×10^{16} hv per sec. This yields 23×10^{13} OH radicals per sec. per cc.

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(7) Warburg, *Sitzb preuss Akad. Wiss.*, 314 (1916).

TABLE I

EXPERIMENTS WITH HYDROGEN

No.	Time of illumination, min.	Initial pressure, mm.	Final pressure with O_2	Final pressure without O_2	H_2O_2 partial pressure, mm.	Speed of gas flow cc./min.	Temp., °C.	Number of H_2 molecules disappearing per sec. per cc.	Number of O_2 molecules formed per sec. per cc.
1	70	712.5	Not measured	709.6	4.0	40	39.0	5.6×10^{13}	Not measured
2	50	711.1	Not measured	709.0	4.0	40	39.0	5.6	Not measured
3	53	729.0	Not measured	724.3	5.1	31	40.7	11.8	Not measured
4	37	725.7	Not measured	723.7	5.1	31	40.7	7.2	Not measured
5	55	735.9	Not measured	734.1	5.1	25	40.3	4.4	Not measured
6	60	784.6	Not measured	780.0	3.4	28	40.1	10.3	Not measured
7	30	723.9	726.5	722.7	5.1	31	40.5	5.4	17.1×10^{13}
8	54	722.7	725.5	721.2	5.1	31	40.5	3.8	10.8
9	55	715.6	721.2	712.8	5.1	25	40.5	6.8	20.5
10	55	701.1	Not measured	700.0	2.0	25	29.0	2.7×10^{13}	Not measured
11	62	772.4	Not measured	771.3	1.7	25	28.0	2.4	Not measured
12	60	772.4	Not measured	740.1	1.7	28	28.3	5.2	Not measured
13	55	697.3	700.6	695.6	2.0	23	27.5	4.2	12.4×10^{13}

EXPERIMENTS WITH CARBON MONOXIDE

No.	Time of illumination, min.	Initial pressure, mm.	Final pressure with O_2	Final pressure without O_2	H_2O_2 partial pressure, mm.	Speed of gas flow cc./min.	Temp., °C.	Number of CO molecules disappearing per sec. per cc.
15	60	706.0	Not measured	702.0	4.0		39.7	9.0×10^{13}
16	60	702.7	Not measured	700.4	2.0		26.8	4.6

Discussion

As mentioned before. reactions **(3)** and **(5)** provide a scheme for the reactions subsequent to the OH formation. If this scheme is true the disappearance of hydrogen would then be accounted for by (3), while a certain excess of OH should disappear unnoticed according to (5). The formation of oxygen requires some special consideration. One might consider the reactions

$$OH + OH = H_2O + O \qquad (6)$$
$$H_2O_2 + O = H_2O + O_2 \qquad (7)$$
$$O + O + M = O_2 + M \qquad (8)$$

of which **(6)** has been proposed by Bonhoeffer and Pearson.[8] This reaction **(6)** cannot be applied to the present experiment without interfering with Frankenburger and Klinkhardt's scheme. No way is left in their scheme for an appreciable consumption of OH according to (6), which means that collisions of OH among themselves must be largely ineffective, so ineffective that three-body collisions according to *(5)* dominate. This is perfectly consistent with the experimental facts of Bonhoeffer and Pearson.[5] Also in the present experiments reaction **(6)** cannot play a role if Frankenburger and Klinkhardt's scheme is true, because the hydrogen concentration and temperature were about the same as in their experiments and the relation between the number of two-body and three-body collisions must be the same as in their experiments.

Another reaction in which oxygen may be formed is

$$OH + OH + H_2O_2 = 2H_2O + O_2 \qquad (9)$$

But this reaction, however plausible, would not fit in the scheme either, because three-body collisions would occur much more frequently with hydrogen molecules than with hydrogen peroxide molecules since the concentration of the former is higher by the order of 10^2. Thus, reaction **(5)** would suppress reaction (9) completely.

As far as the author can see, **all** oxygen forming reactions are now disposed of[9] save those in which OH remains unaffected as, for example

$$OH + H_2O_2 = H_2O + O + OH \qquad (10)$$

This reaction, which would be analogous to the conversion of para to normal hydrogen by hydrogen atoms, would be endothermic, but there is an excess of energy of the dissociating light quanta, forming rather "hot" OH radicals. Another possibility might be

$$OH + H_2O_2 + H_2O_2 = 2H_2O + O_2 + OH \qquad (11)$$

The point is that by applying the Frankenburger–Klinkhardt scheme the oxygen formation in the present experiments must be considered as due to a kind of catalytic decomposition of hydrogen peroxide and not involving the disappearance of OH radicals. If the Frankenburger–Klinkhardt scheme holds, these radicals can only disappear according to **(3)** and **(5).**

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(8) Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).

(9) Compare the discussion of this subject in Bonhoeffer and Pearson's paper.

The rate of OH formation according to (1) per sec. per cc. can be symbolized by $+\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(1)}$, of OH disappearance according to (3) and (5) by $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(3)}$ and $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(5)}$. Then for the stationary state

$$\frac{+\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(1)} = \frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(3)} + \frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(a)} \qquad (12)$$

$+\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(1)}$ equals twice the amount of $h\nu$ absorbed per sec. per cc. and is, therefore, determined by the hydrogen peroxide concentration and the light intensity. $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(3)}$ equals the number of hydrogen molecules disappearing per sec. per cc., or the number of successful binary collisions $\mathrm{OH} + \mathrm{H}_2$, given by the equation

$$\frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = Ze^{-Q/RT} = 2N_{\mathrm{H}_2}\, N_{\mathrm{OH}}\, \sigma_{1,2}^2 \sqrt{2\pi RT\,\frac{M_1 + M_2}{M_1\,.\,M_2}} \qquad (13)$$

N_{H_2} = number of H_2 per cc. = 22.1×10^{18} for $p_{\mathrm{H}_2} = 71$ cm., $t = 40$°C.
N_{OH} = number of OH per cc.
$\sigma_{1,2} = 2.3 \times 10^{-8}$ [4]
$R = 8.313 \times 10^7$

$-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(5)}$, the rate of recombination of OH to hydrogen peroxide, cannot be observed directly. It equals the number of ternary collisions (5) per sec. per cc., and is estimated by Frankenburger and Klinkhardt in the usual way (for atmospheric pressure) as 10^{-4} times the number of binary collisions $\mathrm{OH} + \mathrm{OH}$. The value is $2.77 \times 10^{-15}\, N_{\mathrm{OH}}^2$ binary collisions per sec. per cc. This (their) value can, therefore, be used here because the hydrogen concentration is about the same and the temperature dependency so small as to be negligible in this rough calculation.

For the following calculations an accuracy of a factor ten is quite sufficient for this value of the number of ternary collisions.

Equation (12) becomes

$$\frac{+\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = 7 \times 10^9\, e^{-Q/RT}\, N_{\mathrm{OH}} + 2.77 \times 10^{-15}\, N_{\mathrm{OH}}^2 \qquad (14)$$

and

$$7 \times 10^9\, e^{-Q/RT}\, N_{\mathrm{OH}} = -\,\mathrm{d}[\mathrm{H}_2]/\mathrm{d}t \qquad (15)$$

Taking experiment No. 9 as a specific example and assuming that 23×10^{13} OH are formed per sec. per cc., one obtains from (14)

$$23 \times 10^{13} = 7 \times 10^9\, e^{-Q/313\,R}\, N_{\mathrm{OH}} + 2 \times 2.77 \times 10^{-15}\, N_{\mathrm{OH}}^2$$

and from (15)

$$7 \times 10^9\, e^{-Q/313\,R}\, N_{\mathrm{OH}} = 6.8 \times 10^{13}$$

After elimination of N_{OH}, Q turns out to be 14,780 cal.

Now, if in experiment No. 9, the partial pressure of hydrogen peroxide were 2 mm. instead of 5.1 mm., the light absorption would be only 4.5×10^{13} $h\nu$ per sec. per cc. corresponding to 9×10^{13} OH formed per sec. per cc. If at the same time a temperature of 28° is assumed, instead of 40.5°, equations (14) and (15) change to

$$9 \times 10^{13} = 6.9 \times 10^9\, e^{-14{,}780/301\,R}\, N_{\mathrm{OH}} + 2 \times 2.77 \times 10^{-15}\, N_{\mathrm{HO}}^2$$

and

$$6.9 \times 10^9 e^{-14,780/301\,R} N_{OH} = -\,d[H_2]/dt$$

After elimination of N_{OH} and employing the value of Q derived above one obtains for the number of hydrogen molecules disappearing per sec. per cc. the value 1.87 X 10^{13}.

This value, which should be right for 28° and 2 mm. water pressure, is less than one-third of the value 6.8 × 10^{13} found experimentally for 40° and 5.1 mm. hydrogen peroxide pressure. This large difference holds not only for the above specific example but for all corresponding experiments in Table I. Furthermore, the result is only slightly dependent on assumptions concerning the three-body collision frequency and on errors in the assumed rate of OH formation. The three-body collision frequency might be wrong even by a factor ten without an appreciable change in the above result. The rate of OH formation might have been overestimated, but even if in the above example a value of 7.7 × 10^{13} instead of 23 X 10^{13} is taken—which would just be reconcilable with a value of 14,000 cal. for *Q*—the hydrogen consumption would be altered only to 2.5 X 10^{13} molecules per sec. per cc. It appears, therefore, that for the present experiments, if a change of the hydrogen peroxide pressure from 5 mm. to 2 mm. and of the temperature from 40 to 28° is made, the rate of hydrogen disappearance should decrease to one-third or less, if the proposed reaction scheme holds. This is obviously not in agreement with the facts. The above specific example, experiment No. 9, may properly be compared with experiment No. 13, because they were run one immediately after the other, thus, ensuring similar conditions. In No. 13 a rate of 4.2 X 10^{13} hydrogen disappearing was found, which corresponds to a decrease to two-thirds rather than one-third of the rate of No. 9. But besides this specific case, the decrease in the rate generally in all the experiments corresponds to certainly not more than a half, the mean value in group one being 7.2 X 10^{13} H_2 per cc. per sec. and in group two 3.6 × 10^{13} H_2 per cc. per sec.

From the above it can be concluded that the scheme consisting of reactions (1), (3) and (5) should be discarded. In the opinion of the author, the experiments and calculations are sufficiently accurate to justify this statement. On the other hand, it seems to be difficult to ascertain what has to be eliminated.

From the work of Urey, Dawsey and Rice it seems to be fairly well established that $H_2O_2 + h\nu = 2OH$. If this cannot be disputed, objections may be raised only against the occurrence of reaction (3) and (5). The reaction (3), ($OH + H_2 = H_2O + H$), however, seems to be most plausible for explaining the actually observed disappearance of hydrogen. It seems, therefore, that the reaction which is most probably at fault is reaction (5), $OH + OH + H_2 = H_2O_2 + H_2$. However, no other facts are published in the literature which might lead to objections against reaction *(5)* except this process of elimination. As already pointed out by von Elbe and Lewis[5] the paper of Bonhoeffer and Pearson does not contain any experimental material contradictory to Frankenburger and Klinkhardt's conclusions.

With reaction (5) discarded, an explanation for the formation of hydrogen peroxide is still to be sought. Marshall[10] some time ago proposed the intermediate formation of HO_2. While there is no experimental evidence for this, there is certainly no evidence against it.

In the present experiments the following scheme can be proposed

$$H_2O_2 + h\nu = 2OH \qquad (1)$$
$$OH + H_2 = H_2O + H \qquad (3)$$
$$OH + OH + H_2O_2 = 2H_2O + O_2 \qquad (9)$$

Perhaps this is a plausible scheme, as a rough calculation indicates. If for ternary collisions (9) a similar expression is used as for ternary collisions (5) previously, it follows that Q for reaction **(3)** equals 16,000–17,000 cal., and that the rates of hydrogen consumption and oxygen formation in both groups of experiments change by about one-half. It is hoped, however, that further experiments will allow more definite conclusions to be drawn on the subject.

Summary

3. Mixtures of hydrogen peroxide vapor and hydrogen or carbon monoxide were exposed to the light of a zinc spark. The kinetics of the reaction between the assumed product of dissociation—namely, OH—and hydrogen or carbon monoxide was studied at different partial pressures and temperatures.

2. The results do not sustain the reaction scheme of Frankenburger and Klinkhardt involving the recombination of two OH to hydrogen peroxide. However, there are no facts available which disturb the Bonhoeffer–Haber mechanism for the formation of water from hydrogen and oxygen.

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[10] Marshall. J. *Phys. Chem.*, 30, 1078 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Study of the Catalytic Properties of Bright Platinum and Iridium Deposits in the Activation of Hydrogen[1]

BY LOUIS P. HAMMETT AND ARTHUR E. LORCH

While there are many reasons for believing that quality of surface is at least as important as quantity of surface in determining the activity of a contact catalyst,[2] it has been in practice extremely difficult to separate these variables, and indeed to standardize conditions so that catalysts of reproducible properties may be obtained. The prospect of so doing was, however, considerably advanced by the discovery[3] that smooth bright surfaces of the platinum metals, surfaces therefore of an area as definite as may be hoped for on a solid metal, may be obtained which are very effective for the catalytic activation of hydrogen. The present study is concerned with the determination and investigation of those factors which affect the catalytic properties of electro-deposited platinum and iridium and especially the decrease in activity which occurs when such catalysts are exposed to the activated substance hydrogen.[3]

Measurement of Activity.—Catalytic activity was determined by measuring the specific rate of the electrochemical reaction

$$H_2 \rightleftharpoons 2H^+ + 2e$$

by determination of the polarization of an electrode carrying the catalyst. By means of the apparatus shown in Fig. 1 current–potential curves were obtained, the potential E being measured by a Leeds and Northrup Type K potentiometer, and the current by determination of the potential drop across a known resistance in the circuit. The slope of these curves at the point of zero current, in amperes per volt, and for a gross area of 1 sq. cm. at 25° is reported as the catalytic activity. Since there is no discontinuity of slope at the equilibrium potential, it is immaterial whether the slope be determined by experiments in which hydrogen is oxidized (ΔE and I positive), as is the case with most of the results here reported, or by experiments in which hydrogen ion is reduced.

Our interest being principally in the comparison under identical conditions of electrodes of different preparation, we designed the apparatus to hold *as* many as ten electrodes closely and equivalently grouped around the salt bridge outlet, and used only the gentle stirring furnished by the hydrogen stream at a rate of two or three bubbles a second. The gain

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[1] This article is based upon part of the dissertation submitted by Arthur E. Lorch to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1932.

[2] See for instance the discussion in Taylor's "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, Vol. II, pp. 1088–1089.

[3] (a) Beans and Hammett, THIS JOURNAL, 47, 1215 (1925); (b) Hammett, *ibid.*, 46, 7 (1924).

in comparability of results more than compensates for the loss in precision of the measurement of absolute activity which is implied by the omission of a capillary extension of the salt bridge and by the greater effect of concentration polarization. Values of activity greater than 0.01 ampere per volt/sq. cm. are reproducible to 5 or 10%, and might be increased by very efficient stirring as much as several thousand per cent. To such figures only slight significance can be attached. Below about 0.005 the values are reproducible to about 1% and are altered only a few per cent. by increase in stirring rate.

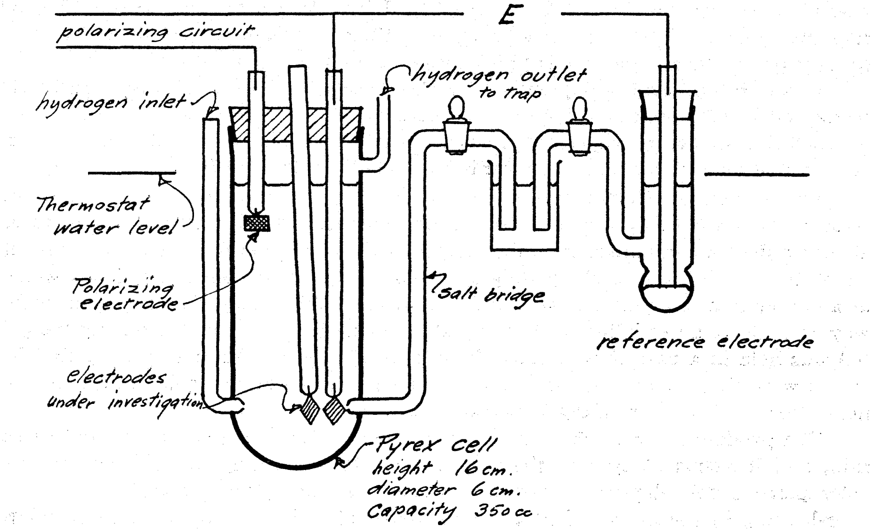

Fig. 1.

Materials.—Hydrogen was prepared by electrolysis of 30% sulfuric acid which was tested and found free from arsenic. The cathode consisted of a large copper sheet and the anode of a lead rod, the material for the latter having been specially freed from arsenic by fusion with lead chloride. The use of sulfuric acid as electrolyte eliminates the nuisance of fine spray, as when alkali is used, and in addition makes possible the continuous service of the generator for many months without appreciable solution of the electrodes. With the low currents used (0.05 to 0.5 ampere per sq. dm.) little if any reduction of sulfate ion occurs. In the purification we have especially guarded against traces of hydrogen sulfide, of sulfur dioxide, of arsine, and of lead hydride[4] as well as against oxygen. In the hydrogen line were placed long columns of cotton and soda lime, heated copper gauze, calcium chloride or "hydralo," and a coil immersed in liquid air. Rubber deteriorates in a hydrogen atmosphere, and emits foul-smelling products which we found to poison the catalysts. The stopper in our cell was a cork well soaked in paraffin wax, capped over with wax and painted with shellac when in place. Only one rubber connection was used in the hydrogen line, and in this a fresh piece of tubing was used in each experiment, and was protected from the hydrogen.

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[4] Paneth and Nörring, *Ber.*, 53, 1693 (1920).

Water was twice distilled through a tin condenser and was stored in non-sol bottles. Hydrochloric acid was distilled in Pyrex glass.

Chloroplatinic acid was prepared by dissolving the metal in aqua regia followed by two precipitations with ammonium chloride, the precipitate being ignited each time and redissolved in aqua regia. The final solution was freed from nitrates by ten to fifteen evaporations to dryness with hydrochloric acid on a steam-bath.

Chloroplatinous acid was prepared by heating chloroplatinic acid at about 300° for one hour, and dissolving the residue in hydrochloric acid to give a solution about one molar in hydrochloric acid and with 1 to 5% of chloroplatinous acid.

"Iridium tetrachloride" from two different sources was used with equivalent results. The most likely composition for the substance usually sold as iridium tetrachloride seems to be about $IrCl_{3.8}\cdot 1.6HCl\cdot 4.5H_2O$.[5] At least it is essentially quadrivalent iridium. Tests on a small sample by the methods of Noyes[6] showed that the proportion of other noble metals present was certainly less than 3%.

Chloroiridous acid was prepared by the method of Délépine,[5] the tetrachloride being boiled with dilute alcohol in acid solution until metallic iridium began to form. The solution was then evaporated to dryness, and the residue dissolved in hydrochloric acid to give a solution about one molar in hydrochloric acid and with 1 to 3% of H_3IrCl_6.

Preparation of Electrodes.—A gold foil 0.65 cm. square free from etching and scratches was used as the base for the electro-deposit. It was found necessary to cut all electrodes for comparison from the same piece of foil in order to ensure approximately equal areas as a base for the plating operation. The square piece of foil was welded at a comer to a fine platinum wire and this was sealed into soft glass tubing in such a way as to leave a negligible amount of platinum exposed. During the sealing the gold foil was held in a pair of tweezers to keep it from melting. Prior to plating the electrodes were thoroughly cleaned (a few minutes in warm chromic acid) to ensure even deposition. This is especially important when using low current densities.

The production of bright deposits from chloroplatinic acid is difficult and uncertain, and it seems likely that the favorable results previously found[3] with purified chloroplatinic acid depended upon the presence of chloroplatinous acid produced by over-heating in the evaporation of the chloroplatinic acid. In the absence of chloroplatinous acid we now find that high current densities lead to grayish or spongy deposits and low current densities lead to no deposit.

A plating bath of chloroplatinous acid, on the other hand, gives brilliant deposits over a wide range of current densities. Since we have found that the presence of small amounts of oxidized material during the plating greatly affects the activity of both platinum and iridium catalysts, and since it decreases the current efficiency, we have used a U-shaped plating cell in which anode and cathode compartments were separated by a plug of filter paper. When working with low current densities we have excluded oxygen by bubbling nitrogen through the cathode compartments and by providing the gas outlet with a trap.

The current efficiency of the deposition of platinum was determined as follows. A piece of gold foil was carefully cleaned, heated to redness, weighed, then very loosely welded to a platinum wire which was sealed into a glass tube. The gold foil was cleaned again and half immersed in the plating bath so that no metal could be deposited near the platinum wire. The plating current was accurately measured at short time intervals by means of a potentiometer and known resistance. The finished deposit was

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[5] Délépine, *Ann. chim.*, [9] *7*, 277 (1917). See also Kraus and Gerbach, *Z. anorg. allgem. Chem.*, *147*, 265 (1925).

[6] Noyes, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927.

washed thoroughly and the gold foil was pulled away from the platinum wire. A blank experiment showed that with the proper technique this could be done without any measurable loss in the weight of the gold foil. After careful washing the gold foil and platinum deposit were heated to red heat and then weighed again. Weights, balance and current measuring devices (resistance and potentiometer circuit) were very carefully checked to ensure the reliability of the results. These are given in Table I.

TABLE I

Wt. of Pt deposit, mg.	Time of plating	Average current, ma.	Plating efficiency of current on basis $Pt^{++} \longrightarrow Pt$, per cent.
20.93	**6** hrs. **0** min.	**0.900**	**106.7**
16.43	**7** 0	.590	**109.5**
24.90	**12** 6	.537	**105 5**

The experimental errors connected with these determinations are estimated as less than one per cent. We can explain these results either by assuming that a tremendous amount of adsorption takes place on the platinum or by assuming the existence of monovalent platinum in the solution. It seems most likely that the latter is the correct assumption. The existence of monovalent platinum has been suggested by several investigators,[7] but is not generally accepted.

Chloroiridic acid solutions give bright deposits over a wide range of current densities, but the current efficiency is low, and we have not been able to obtain reproducible catalytic activities.

Chloroiridous acid solutions give bright deposits at current densities from **0.05** to **50** milliamperes per square centimeter when the solution is stirred. We have not measured directly the current efficiency but the assumption that the thickness of a layer of iridium required to just conceal the color of the gold base is the same as that of a platinum deposit of the same covering power leads to values between **90** and 100%. The conclusion that the efficiency is high and constant is supported by the reproducibility of the catalytic properties of the deposits.

Reproducibility of Catalytic Activity and Life.—In Fig. 2 we have the results of a test of the reproducibility of the preparation of bright iridium catalysts from chloroiridous acid solutions. The six catalysts in question were prepared in the order of their numbers at a current density of 0.418 milliampere per square centimeter over a period of twenty-five minutes. After washing they were introduced into 0.1 molar hydrochloric acid in the cell of Fig. 1, which was placed in a thermostat at 25°, the hydrogen current was started, and the activity was determined from time to time. In the figure the logarithm of the activity is plotted against time. It will be noted that with the exception of number 1, the catalysts are very nearly identical in their activity-life curves. The deviating behavior of number 1, a type of behavior which we have consistently found with the first electrode or two prepared from a fresh solution, is probably to be ascribed to the presence in the solution of quadrivalent iridium, which we have found to give catalysts of slower decay.

[7] Lea, ***Z. anorg. Chem.*, 8, 121** **(1895);** Sonstadt, *Proc. Chem. Soc.*, ***14, 25*** **(1898);** Wohler and Streicher, ***Ber.***, 46, **1.591** ***(1913);*** Wohler and Balz, Z. ***anorg.*** *allgem. Chem.*, ***149, 353*** **(1925).**

In Fig. 3 are given the results of a similar test with platinum, the catalysts being bright platinum plated in the order of their numbers from chloroplatinous acid solution for thirty minutes at a current density of 0.80 milliampere per square centimeter. The reproducibility of properties, while not so good as with iridium, is still excellent for a contact catalyst.

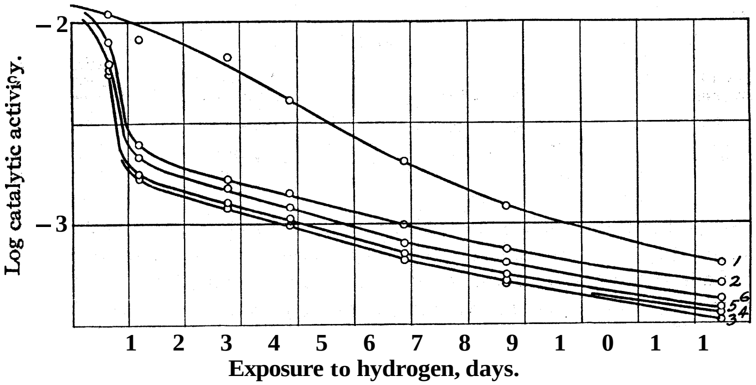

Fig. 2.

We have found that differences in temperature during the plating of as much as 10° have a negligible effect upon catalytic properties.

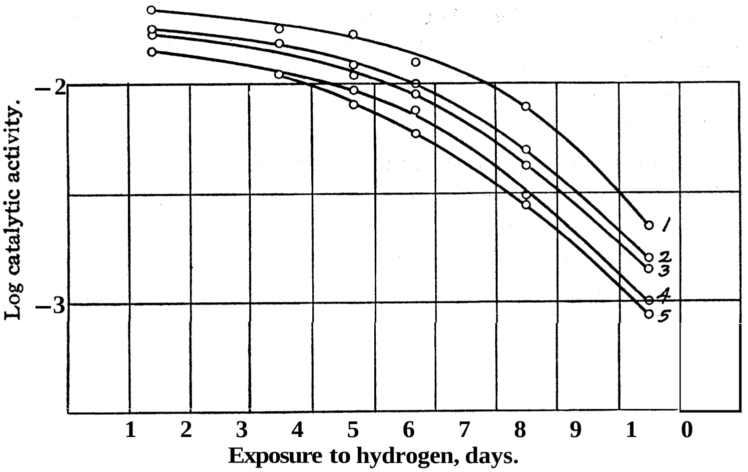

Fig. 3.

The Nature of the Decay in Catalytic Activity.—The decay in activity in a hydrogen atmosphere may be explained in terms of (1) reversion of active and unstable atoms or atomic groupings on the surface to less active states, a process inhibited by the presence of adsorbed oxygen, and accelerated by hydrogen only because of the removal of this inhibition; (2) a relation between the activation of hydrogen and the exhaustion of the catalyst; (3) a poisoning of the catalyst occurring only when the protecting layer of oxygen is removed by hydrogen.

We reject the third explanation on the basis of the following considerations. The very carefully purified hydrogen used in these experiments produces a decay qualitatively identical with that produced in earlier work by commercial tank hydrogen and by hydrogen made in the laboratory by electrolysis of sodium hydroxide solutions with nickel electrodes. The omission of the liquid-air trap in our hydrogen train produced no measurable change in the rate of decay. The known poison, hydrogen sulfide, is reversible in its effect, the activity increasing when the poison is removed; and the decrease in activity produced by saturated hydrogen sulfide solution is less than that produced on long aging in the presence only of the purest hydrogen, water, and hydrochloric acid. In further experiments a number of tubes containing hydrogen were sealed with two platinum electrodes apiece. The electrodes were variously exposed in these tubes. Some were immersed in 0.1 *N* hydrochloric acid, some in pure water, some in water which had never been in contact with glass. The tube in this latter case had been coated with paraffin and the water had been distilled through a tin condenser directly into the tube. Some electrodes were kept entirely out of the solution, being suspended above it in the hydrogen atmosphere. In all these cases the rate of decay of the catalysts was the same, within the limits of experimental error. These limits, it must be admitted, are somewhat wider than those prevailing in other sections of the work, since measurements can only be obtained on the catalysts by transferring them to a cell, a process which causes them to be reactivated to some extent by the air.

Either of the other explanations implies that the decay in activity which takes place at elevated temperatures under any conditions[8] is related to that which we observe at room temperature. This suggests that there should be a difference in the rate of this so-called sintering at elevated temperatures according to the environment, that hydrogen should have a catalytic effect upon the sintering. Such an effect is shown by the experiments described in Table II. In these, eight platinum catalysts prepared so as to be as nearly identical in properties as possible were heated in a Pyrex tube under various conditions, and were then transferred to the cell of Fig. 1. After a lapse of three days in hydrogen in the cell to allow the effects of the temporary activation by the air during the transfer to wear off, the activities were determined. Similar experiments at other temperatures confirm the conclusion that hydrogen does indeed accelerate the decay in activity over a wide range of temperatures.

[8] Vavon, *Compt. rend.*, 158, 409 (1914); Wright and Smith, *J. Chem. Soc.*, *119*, 1683 (1921); Smith, *ibid.*, 123, 2088 (1923); Taylor, *Proc. Roy. Soc.*, (London) A108, *106* (1925); Constable, *J. Chem. Soc.*, 1578, 2995 (1927); Bowden and Connor, *Proc. Roy. Soc.*, (London) A128, 317 (1930).

Effect of Thickness of Deposit and of Rate of Plating.—Figure 4 shows the life curves of five iridium catalysts of different thickness. These were plated for varying times at the same current density (0.27 ma./sq. cm.) from the same solution of chloroiridous acid in the order of the numbers attached to the curves. The average thickness of the deposit calculated on the basis of 100% current efficiency is given in the figure. Figure 5

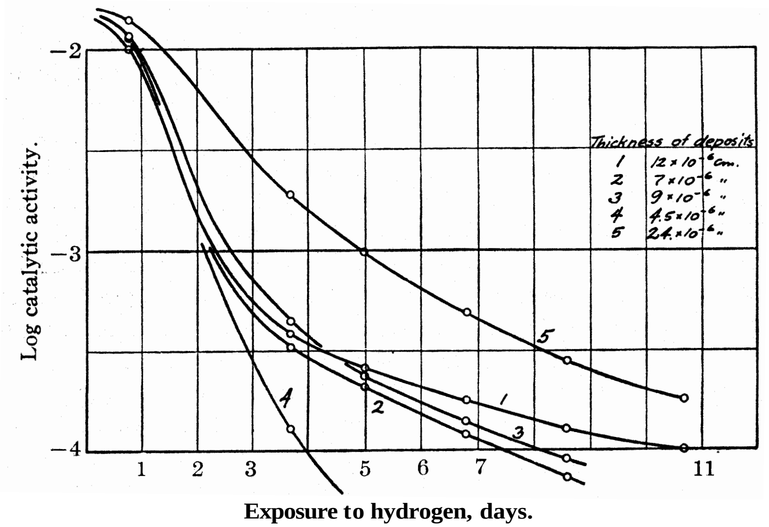

Fig. 4.

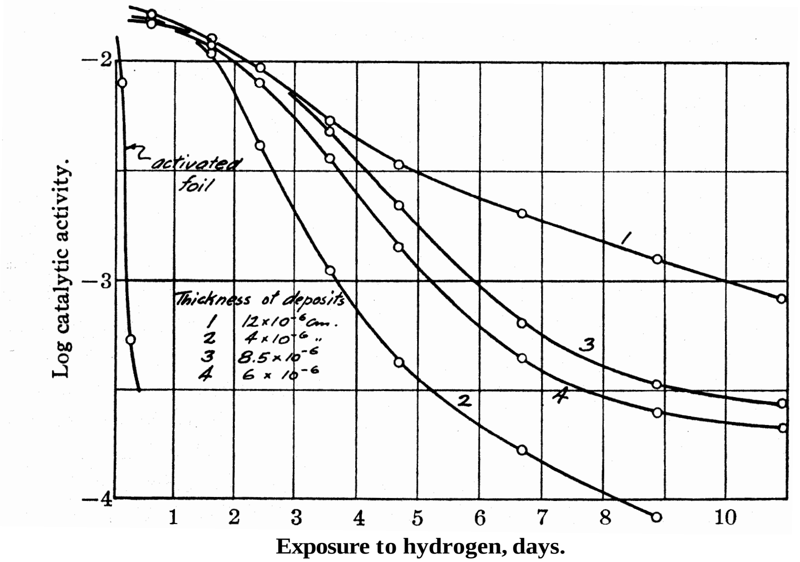

Fig. 5.

TABLE I

		Catalytic activity (a)	 (b)
Group I	No treatment	0.0080	0.0072
Group IV	Placed in dry tube. Air displaced by N_2 and this by H_2. Catalysts heated in H_2 for 1/2 hour at 350°C. H_2 then displaced by N_2 and tube opened	.0000045	.0000015
Group V	Placed in dry tube. Air displaced by N_2 (free from O_2) and tube heated for 1/2 hour at 350°	.000084	.00015
Group VI	Heated in oxygen for half an hour at 350°	.000041	.0018

TABLE II

Order of plating	1	2	[illegible]	4	5	6	7	8	9	10
Time of plating, min.	30	30	[illegible]	15	10	8.5	76	135	175	9.75
Current density ma. per sq. cm.	0.405	0.405	0.405	0.875	1.52	3.38	0.167	0.115	0.0892	8.25
Time for concealment of gold base, min.	7	7	6	3.5	2.5	2	15	30	40	2.25
Estimated thickness:[a]										
Assuming constant 100% current eff., cm.	2.1 × 10	21	2.1	2.2	2.7	5.1	2.2	2.7	2.7	14.0
From time to conceal base, cm.	2.1×10^{-5}	21	2.4	2.1	2.0	2.1	2.4	2.2	2.1	2.1
Exposure, days	Catalytic activity									
0.6	0.0105	0.0125	0.0113	0.0135	0.0109	0.0102	0.0115	0.0132	0.0146	0.0133
1.5	.0090	.0098	.0087	.0092	.0087	.0066	.0089	.0087	.0097	.0088
3.6	.0028	.00150	.00145	.00089	.0016	.00085	.00112	.0030	.00130	.00146
4.7	.00100	.00044	.00049	.00027	.00049	.00025	.00032	.0017	.00068	.00050
6.5	.00023	.00020	.00021	.000119	.000128	.000101	.000145	.00081	.00036	.00017
8.6	.000117	.000103	.000115	.000064	.000054	.000052	.000085	.00037	.00018	.000073

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[a] Due to a miscalculation the figures for thickness given in the thesis upon which this article is based were in error by a constant factor of 0.7.

contains the results of similar experiments with platinum catalysts obtained from a solution of chloroplatinous acid at a current density of 0.141 ma./sq. cm. Similar results have been obtained in other experiments, and we conclude that for electrodeposited platinum and iridium catalysts of equal gross area the catalytic life is greater the thicker the deposit.

The decay curve for an ordinary platinum foil activated by anodic oxygen evolution for five minutes is included in Fig. 5, and shows a very rapid decay rate. This is further confirmation because such an activation should produce only a very thin active layer.

In Table III are given the results of an experiment designed to test the effect of rate of deposition upon the properties of iridium catalysts. The catalysts were all prepared from the same 3% chloroiridous acid solution in the order of the numbers, and it was attempted to make them all of the same thickness by varying the rate of deposition in inverse proportion to the time of plating. The first three were plated at the same rate and the agreement of properties between 2 and 3 shows that the bath had reached a steady condition. The thickness calculated on the basis of constant 100% current efficiency is given and, as a check, the value calculated from the time required to just conceal the color of the gold base. The agreement is excellent except in the case of the two electrodes plated at the highest current densities, and we have discarded the results on these. The accepted results are plotted in Fig. 6, from which it is clear that the best iridium catalysts are those plated at the lowest rate.

Figure 6 also contains the life curve of a catalyst prepared from an iridium tetrachloride solution, and estimated from the time required to conceal the gold base to be somewhat less in thickness than the other catalysts included in the figure. Because of the low current efficiency prevailing in such solutions, this required a current of 0.26 ma./sq. cm. for five and one quarter hours. The characteristically long life may be due to a specific effect of the oxidized iridium as a source of the deposit or possibly to the very slow rate of deposition.

With platinum the difference in properties arising from variation in rate of deposition is certainly smaller than with iridium, and it is difficult to be certain whether any such effect exists, especially in view of the poorer reproducibility of platinum catalysts.

Both the effect of thickness of deposit and the effect of rate of deposition are not obvious conclusions from usual theories of contact catalysis. All of the catalysts for which we have here given results appeared perfectly smooth and lustrous to the naked eye or under magnification of 750 diameters. Nevertheless the quantity of metal required to conceal the color of the gold base corresponds to a thickness of from 1 to 2.5×10^{-6} cm. or about 40 to 100 atomic layers. This suggests that crystal growth starts from centers scattered over the surface of the gold and proceeds laterally as well as upward until adjacent crystals touch. The surface of the deposit might then be expected to have a saw-tooth cross section with a tooth height of some 80 to 200 atom diameters. Since, however, an increase in thickness beyond that required to obscure the base results in increased catalytic life, it must be supposed that fissures or pores much deeper than the average depth of the saw-teeth exist, and have a very marked effect upon catalytic properties.

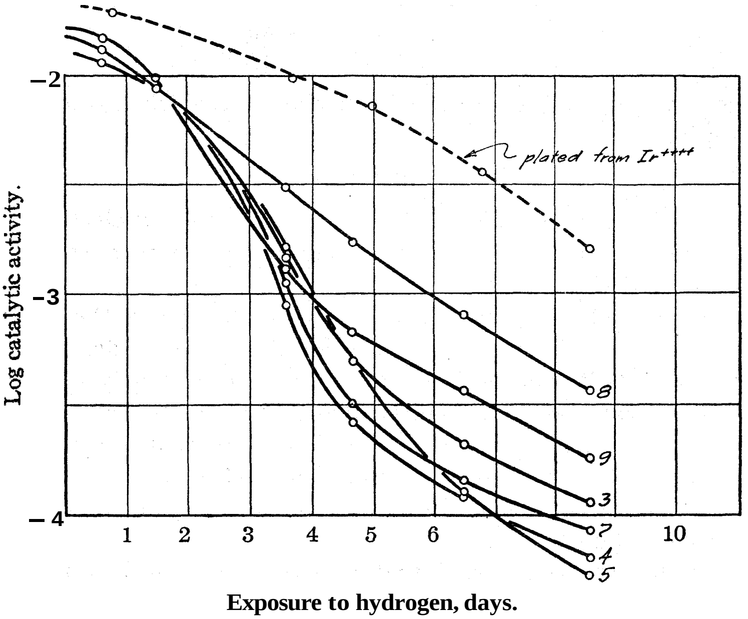

Fig. 6.

All of the curves show an initial rapid decay whose rate is very nearly the same in all cases. This initial decay is therefore independent of the thickness of the deposit and is to be attributed to the loss in activity of that part of the catalyst in which all these catalysts are identical, the ordinary or external surface. It is only after this, which furnishes most of the initial activity, has decayed that the properties of that part of the catalyst which depend upon thickness become significant. Furthermore, the differences in slope of the later parts of the curves in Figs. 4 and 5 indicate that thicker deposits lead to inner surfaces (of the fissures or pores) whose specific rate of decay is smaller, whereas the parallelism (on the semilogarithmic plot) of the later part of the curves in Fig. 6 suggests that differences in rate of deposition result in differences in activity of the inner surface but not in the fractional loss of activity in unit time.

In other words, the external surface, which is the most exposed to hydrogen, decays most rapidly, and of the inner surfaces, those present in the thicker deposits, and therefore least accessible to the hydrogen, decay at the lowest rate. This experimental conclusion may also be derived as a corollary from Tanner's recent theory of contact catalysis,[9] according to which activation depends upon the existence of local excesses in temperature at the active points. It follows that contact with and consequent activation of the reactant should tend to produce decay of the catalyst and that those areas which are most exposed to hydrogen and on which the reversible reaction

$$2H^+ + 2e \rightleftharpoons H_2$$
$$\text{or} \qquad 2H \rightleftharpoons H_2$$

proceeds at the greatest rate should be those on which loss of activity is most rapid.

Summary

Methods have been perfected for the preparation by electrodeposition of platinum and iridium catalysts of reproducible properties for the activation of hydrogen.

The loss in activity which such catalysts undergo in the presence of hydrogen at room temperature has been shown to be dependent upon the hydrogen itself and not upon poisons, and to be closely related to the so-called sintering which takes place at higher temperatures.

The dependence of decay upon thickness of deposit and upon rate of deposition has been investigated, and the conclusion reached that these apparently smooth solid deposits have an inner surface of great importance for their catalytic behavior.

Indications have been found that it is the actual activation of hydrogen which is responsible for the decay, and the relation of this conclusion to Tanner's theory of contact catalysis has been pointed out.

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[9] Tanner, THIS JOURNAL, 54, 2171 (1932).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Photo-oxidation of Gaseous Hydrogen Iodide

BY JOHN R. BATES AND GEORGE I. LAVIN

In studies[1] of the reaction of hydrogen atoms with oxygen molecules it has been assumed that the first process consists of an associative reaction between these atoms and oxygen molecules.

$$H + O_2 \longrightarrow HO_2 \qquad (1)$$

The molecule HO_2 then reacts with a hydrogen molecule if a subsequent collision with hydrogen occurs within the lifetime of HO_2 and has sufficient energy.

The straight bimolecular process

$$H + O_2 \longrightarrow OH + O - 13.5\ \text{cal.} \qquad (1a)$$

has been ruled out as improbable, due to the high activation energy necessary. If we accept the values for the heat of formation[2] of OH and O_2 of 104 cal. and 117.5 cal., respectively, the reaction is endothermic 13.5 cal. Only one collision in at least 5×10^{10} would be effective at 0°. However, the value of 104 cal. for OH is not as definite as might be desired, and it is well to note that this mechanism does not agree with the experimental evidence obtained from quantum yield studies of the reaction.

The value of the quantum yield of hydrogen peroxide formation in the sensitized reaction is of the order of 1.2–2.5 as given by the work of Marshall[3] and of Frankenburger and Klinkhardt.[4] Reaction (1a) would give rise to a maximum of but one hydrogen peroxide molecule per quantum, since oxygen atoms are known[5] not to react with hydrogen molecules.

For a considerable time it was assumed that the quasi molecules such as HO_2 could only exist for about 10^{-13} to 10^{-14} seconds. More recently it has been suggested by Kassel[6] and demonstrated experimentally by Pease[7] in the hydrogenation of ethylene that these molecules may have greater lifetimes, especially in cases where the molecule is polyatomic. It seemed, therefore, desirable to see if it was not possible to learn something concerning the lifetime of HO_2 in the reaction of hydrogen atoms with oxygen.

Since hydrogen iodide is known to decompose into atoms[8] on the absorption of a quantum of light it appeared feasible to study the oxidation of hydrogen atoms by the method used in the case of methyl groups[9] and to

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(1) **Bonhoeffer and Haber,** Z. *physik.* Chem., **137A,** 363 (1928); **Frankenburger and Klinkhardt,** *Trans. Faraday Soc.*, '27,431 (1931).

(2) **Haber and Bonhoeffer,** *Z. physik. Chem.*, 127, 264 (1928); **Bonhoeffer and Reichert,** *ibid*, **129A,** 76 (1928); **Herzberg.** *ibid.*, **10B,** 189 (1930).

(3) **Marshall,** J. *Phys. Chem* , **30, 1078** (1926); THIS JOURNAL, 64, 4460 (1932).

(4) **Frankenburger and Klinkhardt,** *Trans. Faraday Soc.*, '27,431 (1931).

(5) **Kistiakowsky,** THIS JOURNAL, 62,1868 (1930).

(6) **Kassel,** *ibid.*, 63, 2143 (1931).

(7) **Pease,** *ibid.*, 64, 1876 (1932).

(8) **Ronhoeffer and Farkas,** *Z. physik. Chem.*, 132, 235 (1928).

(9) **Bates and Spence,** THIS JOURNAL, **53,** 1689 (1931).

obtain from the kinetics of the hydrogen iodide photo-oxidation valuable data concerning the reaction of hydrogen atoms and oxygen molecules.

Experimental

The apparatus was similar to that of Bates and Spence.[9] The same mercury arc and reaction vessel was used, but since hydrogen iodide is corrosive a quartz spiral manometer was substituted for the mercury manometer. Very satisfactory yields of hydrogen iodide[10] were obtained by passing hydrogen over iodine and then over a platinum catalyst. The hydrogen iodide was distilled in *vacuo*, and a pure white product, free from iodine, was obtained. The final product was distilled into a tube which was immersed in liquid air. Oxygen was taken from a tank, dried and stored in a large glass bulb. Since, according to Bodenstein and verified by the present work, hydrogen iodide does not appreciably attack pure vaseline, this was used to lubricate the stopcocks shutting the reaction vessel from the rest of the system,

The quartz reaction vessel was kept at a temperature of 0°. The vessel was connected to the rest of the apparatus by a ground joint so that it could be removed and the reaction products studied.

Experimental Results

A series of runs showed that with oxygen present the pressure decrease was greater than could be obtained by the decomposition of hydrogen iodide alone. In the straight decomposition process **a** decrease equal to half the original hydrogen iodide present is to be expected:

$$2HI \longrightarrow H_2 + I_2$$

In Table I it can be seen that with oxygen present the pressure decrease observed $(-\Delta P_{\text{obs.}})$ is considerably greater than $-\Delta P$ obtained by dividing the original hydrogen iodide pressure by two.

Reaction Products

Iodine.—By titrating with $N/10$ thiosulfate it was possible to show that practically all of the iodine originally present in the hydrogen iodide could be recovered as free iodine. The titrations of iodine are given by $-\Delta HI$ in Table II.

Hydrogen Peroxide.—Since all of the mechanisms postulated for the reaction of hydrogen atoms with oxygen involve the formation of hydrogen peroxide efforts were made to identify it in the products. **A** liquid product, which could be seen in the reaction vessel after a run, was washed out in water and the excess iodine removed with silver nitrate. Such **a** liquid gave very slight tests for peroxide. **A** blank run on iodine dissolved in water gave no such test. It is not surprising that hydrogen peroxide should not appear in large quantities, since Abel[11] has shown that liquid

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(10) Bodenstein, *Z. physik. Chem.*, 29, 296 (1899).

(11) Abel, *ibid.*, 136, 161 (1928).

TABLE I

HI, mm.	02, mm.	$-\Delta P_{(obs.)}$	$-\Delta P$ ($^1/_2$ P_{HI})
53.0	300	35.5	26.5
50.2	493	39.7	25.1
50.2	302	38.3	25.1
49.9	255	34.6	24.9

TABLE II

No.	Initial pressure		Rnal total press.	Corrected final press.	$-\Delta$HI	Final HI (HI_E)	% H_2 G. A.	% H_2 $-\Delta$P	Mm. Hi Final	Mm. H_2 $-AP$	K G.A	K_2/K_1 G. A.	K $-\Delta P$	K_2/K_1 $-\Delta P$
	HI	O_2												
B1	50.4	150 1	168.5	160.0	46.5	3.9	8.3	8.6	13.2	14.0	17.2	0.114	13.2	0.088
B2	50.5	150.5	171.0	162.7	46.8	3.7	8.3	9.6	13.5	15.9	16.5	.110	10.2	.066
B3	50.5	302.3	315.5	309.1	48.7	1.7	4.2	4.1	13.1	12.8	17.8	.059	19.0	.069
B4	50.2	512.5	520.3	512.7	47.2	3.0	1.23, 1.27	1.3	6.3, 6.5	6.7	67, 65	0.130, 0.127	61.0	.119
B5	51.0	199.0	218.0	211.1	48.7	2.2	6.4	7.6	13.6	16.2	17.3	0.087	10.2	.051
B6	49.9	255.7	271.0	263.0	46.5	3.4	5.3	4.6	14.0	12.4	14.3	.056	20.0	.078
C-1	112.3	302.0	349.3	329.7	92.7	19.6	9.6		31.9	33.9	26.0	.084	40.0	.134
C-2	101.1	309.0	348.9	329.9	82.1	19.0	10.4, 8.6		34.3, 28.6	27.6	40.0	.130	25.0	.073
C-3	101.8	269.5	313.4	290.3	78.7	23.0	9.6, 11.0		28.0, 31.9	27.1	17.5	.065	25.0	.093
												Av. 0.095		Av. 0.085

hydrogen peroxide is decomposed in the presence of hydrogen iodide, yielding water and oxygen. The hydrogen iodide acting as a catalyst is not removed by the reaction. Knowing little of the conditions in the liquid phase in our reaction system, we were forced to the assumption that those processes occurring in the liquid phase were without effect upon the gas reactions, an assumption which is perhaps approximate, but which is borne out by the results.

Hydrogen.—Since both decomposition and oxidation were taking place simultaneously, it became necessary to determine the hydrogen formed during the course of the reaction. Accordingly gas analyses were carried out upon the gaseous products resulting from various initial concentrations of reactants. In most cases the hydrogen to oxygen ratio was determined by explosion and by absorption of oxygen by pyrogallol. These data are shown in Table II. Also recorded in the same table are the initial concentrations, the final total pressure and the final pressure of hydrogen calculated from the final total pressure and the gas analyses.

Influence of Oxygen on the Reaction Rate.—The variations of rate of decrease in pressure with varying oxygen pressures were studied, keeping the hydrogen iodide pressure constant. These results are represented in Table III, column 2.

TABLE III

					$K_2/K_1 = 0.097$	
P_{O_2}	No.	A	Rate observed	Rate calcd.	Obs. corrected rates	Calcd. corrected rates
300	A-2	0.76	1.35	1.16	1.35	1.16
401.6	A-7	.61	1.25	1.01	1.56	1.26
101.2	A-5	.61	0.75	0.75	0.935	0.935
302.8	A-9	.599	0.87	0.94	1.11	1.19
611.6	A-11	.45	1.13	0.82	1.91	1.61
149.8	A-18-B	1.28	2.08	1.71	1.235	1.015

Discussion of Results

If we assume that the reaction of hydrogen atoms with oxygen takes place through the formation of the molecule HO_2, *as* seems most probable, we may write the steps of the reaction as follows

$$HI + h\nu \longrightarrow H + I \quad I(1 - e^{-\alpha HI}) = A \qquad (1)$$
$$H + HI \longrightarrow H_2 + I \qquad K_1 \qquad (2)$$
$$H + O_2 \longrightarrow HO_2 \qquad K_2 \qquad (3)$$
$$HO_2 + HI \longrightarrow H_2O_2 + I \qquad K_3 \qquad (4)$$
$$HO_2 \longrightarrow H + O_2 \qquad K_4 \qquad (5)$$

At stationary concentrations

$$\frac{d[H]}{dt} - - \frac{d[H]}{dt} \text{ and } \frac{d[HO_2]}{dt} = \frac{d[HO_2]}{dt}, \text{ or}$$

$$[HO_2]K_4 + A = [HI[HI]K_1 + [H][O_2]K_2, \text{ and} \qquad (I)$$
$$[H][O_2]K_2 = [HO_2][HI]K_3 + [HO_2]K_4 \qquad (II)$$

Equations I and II can be solved simultaneously to give the stationary concentrations of HO_2 and H in terms of [HI], $[O_2]$, A, K_1, K_2, K_3 and K_4.

The rate at which hydrogen is produced according to (2) is

$$\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}t} = [\mathrm{H}][\mathrm{HI}]K_1 \qquad \text{(III)}$$

while the total rate of hydrogen iodide decomposition may be represented

$$-\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{d}t} = 2[\mathrm{H}][\mathrm{HI}]K_1 + 2[\mathrm{HO}_2][\mathrm{HI}]K_3 \qquad \text{(IV)}$$

Dividing III by IV we obtain

$$-\frac{\mathrm{d}[\mathrm{Ha}]}{\mathrm{d}[\mathrm{HI}]} = 1/2\ \frac{[\mathrm{H}][\mathrm{HI}]K_1}{[\mathrm{H}][\mathrm{HI}]K_1 + [\mathrm{HO}_2][\mathrm{HI}]K_3} \qquad \text{(V)}$$

Substituting the values of [H] and $[HO_2]$ obtained from I and II we obtain

$$[\mathrm{H}_2] = -\ 1/2 \int_{\mathrm{HI}_0}^{\mathrm{HI}_E} \frac{([\mathrm{HI}]K_3K_1 + K_1K_4)\mathrm{d}[\mathrm{HI}]}{[\mathrm{HI}]K_3K_1 + [\mathrm{O}_2]K_2K_3 + K_1K_4} \qquad \text{(VI)}$$

where HI_0 and HI_E are the initial and final pressures of hydrogen iodide. If $[O_2] = 0$, we arrive at the expression

$$[\mathrm{H}_2] = 1/2 \int_{\mathrm{HI}_E}^{\mathrm{HI}_0} \mathrm{d}\,[\mathrm{HI}], \text{ or } [\mathrm{H}_2] = \frac{\text{HI decomposed}}{2} \qquad \text{(VII)}$$

which is true for straight photochemical decomposition. The same expression is deduced if $K_4 >> K_1$, K_2 and K_3, which would indicate that, if K_4 is very much greater than the other constants, no oxidation of the hydrogen atoms will occur.

If, on the other hand, we can neglect K_4 in comparison with the other constants we obtain

$$\mathrm{d}[\mathrm{H}_2] = 1/2 \int_{\mathrm{HI}_E}^{\mathrm{HI}_0} \frac{[\mathrm{HI}]K_1}{[\mathrm{HI}]K_1 + [\mathrm{O}_2]K_2}\ \mathrm{d}[\mathrm{HI}] \qquad \text{(VIII)}$$

Integrating, and taking the limits

$$\frac{1}{K} = \frac{1}{\mathrm{HI}_0 - \mathrm{HI}_E - 2\mathrm{H}_2} \ln \frac{K + \mathrm{HI}_0}{K + \mathrm{HI}_E} \qquad \text{(IX)}$$

where $K = (K_2/K_1)[O_2]$.

It appears immediately that K_4 is not sufficiently greater than the other constants to make VII hold. If this were true, we should expect no influence of oxygen on the decomposition of hydrogen iodide, and hydrogen and iodine would be the sole products, which is definitely disproved by the data of Table II.

Equation VI cannot be used in its present form to express the results because of the large number of undetermined constants it contains. It seemed, therefore, most convenient first to attempt to fit the experimental results to IX and then to observe any deviations which might occur in the constancy of K_2/K_1, which would indicate the relative magnitude of K_4 and the other constants. HI_0 is the initial pressure of hydrogen iodide, while

$HI_0 - HI_E$ is given by the iodine titration. whence values for both of these can be obtained. $[H_2]$ can be obtained in two ways, The analysis of the hydrogen and oxygen resulting from the reaction, together with the final total pressures of these gases, gives $[H_2]$ directly. If we assume that the oxidation product of the reaction is water it is possible to obtain the amount of hydrogen present after reaction from the total decrease in pressure and the iodine titration. If γ is the fraction of the hydrogen iodide reacting to give water, $1 - \gamma$ produces hydrogen. If, then, we write the two over-all reactions:

$$2HI \longrightarrow H_2 + I_2, \text{ and}$$
$$4HI + O_2 \longrightarrow 2H_2O + I_2$$

it can readily be seen that the following equation holds

$$\frac{(1 - \gamma)(HI_0 - HI_E)}{2} + 5/4\,(HI_0 - HI_E)\gamma = -\Delta P + 4.6 \text{ mm.}$$

where 4.6 mm. is the vapor pressure of water at 0°. After solving this for γ, $[H_2]$ is obtained from the expression

$$H_2 = \frac{2}{(1 - \gamma)(HI_0 - HI_E)}$$

The values for H_2 obtained from these two sources are found in Table II, columns 7 and 8, labeled H_2 G.A. and $H_2\Delta P$, respectively. Fairly good agreement is obtained between the two values in any one experiment, indicating that water is the final product of the oxidation reaction.

We now have all the values necessary for a determination of K and K_2/K_1 from equation IX. This equation is easiest solved by a method of trial and error. We put $1/K = Y = 1/(HI_0 - HI_E - 2H_2)\ln(K + HI_0)/(K + HI_E)$, and then plot the hyperbola $Y = 1/K$, which is independent of the various experimental values. The point at which $Y = 1/(HI_0 - HI_E - 2H_2)\ln(K + HI_0)/(K + HI_E)$ intersects the hyperbola is the desired solution of K. The values of K are given in Table II. From these, and the initial oxygen concentrations, K_2/K_1 are obtained and given in columns 12 and 14. These values agree among themselves within the limits of these experiments and indicate that we are justified in neglecting K_4 and using equation X to express our results.

It can be seen that the rate of the reaction, that is, $-\mathrm{d}P/\mathrm{d}t$, will be given by

$$-\frac{dP}{dt} = \frac{dH_2}{dt} + 2.5\,\frac{dH_2O_2}{dt} \tag{X}$$

Eliminating [H] and $[HO_2]$ and substituting we have

$$-\frac{dP}{dt} = \frac{A([HI] + 2.5[O_2]K_2/K_1)}{[HI] + [O_2]\,K_2/K_1} \tag{XI}$$

The value of A is found by placing $[O_2] = 0$ and is the rate of decomposition of hydrogen iodide. It is to be pointed out that since it was impossible to maintain a constant (from day to day) light intensity it was always necessary to make parallel experiments with hydrogen iodide alone and then with oxygen. In this way the variation of the light source was minimized and the necessary modification of A obtained.

We are now in a position, having evaluated K_2/K_1, to calculate $-dP/dt$ assuming K_4 to be small, and to compare the value so obtained to the experimental value. In Table III the values of A are obtained from the corresponding runs with hydrogen iodide alone; in column 4 the ratio, calculated from equation XI, and using the A values given in column 2. In the last two columns these values are corrected to an A value of 0.76, thus showing the rise in absolute rate as the oxygen increased. The corrected experimental values agree with the calculated within 20% and are a further proof that our mechanism is correct.

It becomes of great interest to see what restrictions neglecting K_4 in equation VII places upon the magnitude of this quantity. Suppose K_1, K_2 and K_3 are bimolecular constants expressed in millimeters pressure of mercury reacting per second per millimeter pressure of reactants. One atom at one millimeter pressure makes $\sim 10^7$ collisions per second, so that the total number of bimolecular collisions at 1 mm. pressure of reactants is equal to $\sim 10^7 \times 10^{16} = \sim 10^{23}$ per cc./sec. at 1 mm. pressure of the gases. Thus our constants K_1, K_2, K_3 are $\gtrsim 10^{23}/10^{16} = 10^7$ mm./sec. per mm. of reactants. Their true value will be smaller than this figure by a factor giving the efficiency of collisions, which will depend upon activation energy, and steric factors. They cannot, which is of importance for our considerations, exceed this order of magnitude.

If, using $K_1 = K_2 = K_3 = 10^7$, we substitute a value of $K_4 = 10^{13}$, which gives an accepted value for the life of a quasi-molecule equal to 10^{-13} sec., and also substitute for [HI] 50 mm. and [O_2], 200 mm., we find that the amount of oxidation would be of the order of 2 parts in 100,000. The value of $-d[H_2]/d[HI]$ would differ from 0.5 by only 0.02%, indicating that hydrogen would be the sole detectable product. This shows us immediately that such a value for K_4 is much too high, since at these concentrations we observe considerable oxidation (Table I).

Before going further it would perhaps be well if we could arrive at more carefully estimated values for our k's. Bonhoeffer and Farkas[8] have observed that the relative efficiencies of the reaction of hydrogen atoms with hydrogen iodide and iodine are in the ratio 1:100. This means that K_1 must be less than 10^5. Our results show that K_2, on this basis, would be $\sim 10^4$. These values in the expression $([HI]K_1K_3 + K_1K_4)/([HI]K_1K_3 + [O_2]K_3K_2 + K_1K_4)$ give the values shown in Table IV, using $[O_2] = 200$ throughout and the values of $K_3[HI]$ and K_4 indicated. The fraction under $K_4 = 0$ are those which agree with our experiments, and deviations from these values for various K_4 values can be read from the table.

TABLE IV

$O_2 = 200$ mm.

$K_4 =$		0	10^7	10^8	10^9	10^{10}
$K_3 = 10^7$	HI = 50	0.715	0.72	0.75	0.884	0.981
	HI = 10	.333	.354	.500	.925	.990
$K_3 = 10^6$	HI = 50	.715	.75	.884	.981	
	HI = 10	.333	.500	.925	.990	

It can easily be seen that in the most unfavorable circumstances, shown by the top row that K_4 is certainly $\leqq 10^9$. There the deviation from experiment is $(0.884 - 0.715)/0.715 = 23.6\%$. In addition, since our results represent an integration over pressures of hydrogen iodide from 50 to $\sim$3 mm., we can safely say that the value of K_4 is probably 10^8.

The usually accepted values for the lifetime of such a quasi-molecule are of the order of 10^{-13} to 10^{-14} seconds, which give rise to a decomposition reaction constant of 10^{13} to 10^{14}. These values are, then, 10^4 to 10^6 greater than we find in our experiments, and indicate, as suggested by Kassel, that the lifetimes involved in polyatomic quasi molecules are considerably greater than usually accepted. This is of great interest in all cases in which a so-called three-body process is involved, since, when the lifetime increases above a definite value, the reaction loses its three-body characteristics and becomes essentially a straight bimolecular reaction. It also should be recognized that the reverse process of unimolecular decomposition involves considerations which may be affected by this longer lifetime.

It is of interest to discover the significance of these high values of the lifetime of HO_2 in the light of Kassel's considerations. This molecule has a heat of formation from a hydrogen atom and an oxygen molecule of 69 large calories if we take half of the energy of formation of hydrogen peroxide:

$$2H + O_2 \longrightarrow H_2O_2 + 138 \text{ Cal}$$

Further, having three atoms, its "s" value is three. Using these data we find that for $K_4 = 10^9$, n, the number of vibration levels, must be $\sim$50. For $K_4 = 10^8$, $n \sim 100$. These give us average vibrational quanta of 500 cm.$^{-1}$ and 250 cm.$^{-1}$, respectively, provided 0.1 of the energy continuum is to be filled. *A priori,* these are not at all impossible values. It must be remembered that these are only average values. The most fully worked out example of the relation of such an average value to the fundamental frequency of a molecule is given by the upper electronic level involved in the visible iodine absorption bands. Here 59 vibration levels are known within an energy interval of 4400 cm.$^{-1}$,[12] giving a maximum average separation of 75 cm.$^{-1}$. The fundamental frequency of this state is 127.5 cm.$^{-1}$. Remembering that the value 75 cm.$^{-1}$ is obtained by using only the number of measured levels, which is smaller than the actual number,

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(12) Ruark and Urey, "Atoms, Molecules and Quanta," The McGraw-Hill Book Co., New York, 1930, pp. 395, 400, 402. The value 4400 is ohtained by subtracting the energy of the electronic jump from that of the convergence limit.

e can readily see that the average separation is considerably smaller than he fundamental frequency. An examination of band spectra data will eveal that this must be fairly universal. In attempting to compare the alues of 500 and 250 cm.$^{-1}$ with those of the HO_2 molecule, the nearest ossible approach are the fundamental frequencies of hydrogen peroxide,[13] 75 and 903 cm.$^{-1}$. These are not incompatible with the 500 cm.$^{-1}$ average alue, but perhaps high for the 350 cm.$^{-1}$ average.

A consideration of the possibility of the reaction

$$H + O_2 \longrightarrow OH + O \qquad \text{(a)}$$

ccurring in the light of these data yields an interesting fact which makes this process seem unlikely. As we have said, the ratio of the K_b and K_c n the reactions

$$H + I_2 \longrightarrow HI + I \quad K_b \qquad \text{(b)}$$
$$H + HI \longrightarrow H_2 + I \quad K_c \qquad \text{(c)}$$

is 100, $K_b/K_c = 100$. Now reaction (b) is supposed to involve little or no activation energy.[14] Hence, reaction (a) would take place in about 1 in every 1000 collisions, which indicates an activation energy of 3.8 cal. If this were true, the heats of formation of O_2 and OH could not differ by more than this amount, while the difference in the accepted values is 13.5 cal., a discrepancy of 10 large calories.

Since this mechanism seems an unlikely one according to the accepted values for the heats of linkage involved, we are led to the formation of the HO_2 complex as the only plausible explanation of the reaction. In addition to other evidence already discussed earlier in this work, the formation of high percentages (90%) of hydrogen peroxide in the mercury sensitized hydrogen–oxygen reaction also points to the HO_2 intermediate. This reaction has been the subject of intensive work in this Laboratory which will be presented shortly in THIS JOURNAL. The long life ascribed by us to the HO_2 molecule is naturally contingent upon its intermediate formation being the correct mechanism for the reaction studied.

The authors wish to thank Professor Hugh S. Taylor for his many constructive criticisms.

Summary

1. The kinetics of the photo-oxidation of gaseous hydrogen iodide have been studied.

2. The result of the application of simple reaction kinetic theory to the experimental results leads to the conclusion that the quasi molecule HO_2 can have a life of 10^{-8} to 10^{-9} seconds, which is many orders of magnitude larger than that usually ascribed to such complexes.

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(13) Kohlrausch, "Der Smekal-Raman Effect," Table XXII.

(14) Eyring, THIS JOURNAL, 53, 2537 (1931).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY

A Potentiometric Titration Method for Fluorine

BY NELSON ALLEN[1] AND N. HOWELL FURMAN

Introduction

A potentiometric titration of fluorine requires an indicator electrode for fluoride ions or for the substance that is reacting with the fluoride. Since no electrodes are available for the fluoride ion an electrode must be selected which changes its potential with the concentration, or activity, of the ions of the reagent. The fluoride may be precipitated or caused to form a complex ion such as $FeF_6^{\equiv}$ or $AlF_6^{\equiv}$. Treadwell and Kohl[2] were the first to propose a potentiometric method for fluorine, their procedure being based on the formation of $FeF_6^{\equiv}$, a volumetric method which had been previously investigated by Greeff[3] using potassium thiocyanate as a color indicator. Later these two authors made use of aluminum chloride for the titration,[4] the aluminum ions decomposing the iron cryolite complex, and Treadwell and Bernasconi applied the method to the determination of aluminum and magnesium in the presence of each other.[5] In the papers of Treadwell and Kohl the conductimetric titration of pure fluoride solutions with aluminum ions was reported.

The insoluble fluorides are few in number and the precipitation titrations are limited to the formation of the fluorides of the alkaline earths, thorium and the rare earths. Most of the volumetric methods are based on the precipitation of calcium fluoride, although one useful and interesting method involves the titration of chloride secured from lead chlorofluoride.[6] Potentiometric methods depending purely on the precipitation of an insoluble fluoride are still further limited because of the lack of suitable indicator electrodes, and thus far no such methods have been advanced.

Kurtenacker and Jurenka[7] titrated fluoride with cerous nitrate using methyl red as an indicator and their work indicates that cerous fluoride is quite insoluble and very stable. Batchelder and V. Meloche[8] did further work on the titration using methyl red and their work corroborates the statement anent the insolubility of cerous fluoride. The stability of the precipitate is shown by the results secured by Batchelder and V. Meloche using their indirect method for fluorine in which an excess of cerous nitrate is added and the excess determined by potassium permanganate using the method of Lenher and C. Meloche.[9] Thus precipitation of fluoride as

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(1) J. T. Baker Chemical Company Fellow in Analytical Chemistry.

(2) Treadwell and Köhl, *Helv. Chim. Acta*, **8**, 600 (1925).

(3) Greeff, *Ber.*, 46, 2511 (1913).

(4) Treadwell and Köhl, *Helv. Chim. Acta*, *9*, 470 (1926).

(5) Treadwell and Bernasconi, *ibid.*, **13**, 500 (1930).

(6) Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

(7) Kurtenacker and Jurenka, Z. *anal. Chem.*, **82**, 210 (1930).

(8) Batchelder and V. Meloche, Tars JOURNAL, 53,2131 (1931); 64,1319 (1932).

(9) Lenher and C. Meloche, *ibid.*, **38**, **66** (1916).

cerous fluoride seems particularly suited for a potentiometric method provided some electrode can be obtained to serve as an indicator for cerous ions.

Development and Theory of Method.—Unfortunately a cerous–ceric combination cannot be used as an indicator since ceric fluoride is only slightly soluble also, but still more soluble than the cerous salt. A suitable electrode for cerous cerium has been found in an application of the ferri–ferrocyanide electrode.[10]

Cerous cerium has been determined by oxidation with potassium ferricyanide by Tomiček,[11] by precipitation as $Ce_4[Fe(CN)_6]_3$ by Treadwell and Chervet[12] and by precipitation as $CeKFe(CN)_6$ by Atanasiu.[13] Atanasiu performed the titration at 65° in a solution containing 30% ethyl alcohol. A repetition of this work checked his results and it was found possible to determine fluoride indirectly by adding an excess of cerous nitrate and determining the excess potentiometrically with potassium ferrocyanide. However, a direct method was desired and the insoluble $CeKFe(CN)_6$ was used to furnish an indicator electrode for cerous ions in the following manner. Kolthoff[14] employed a mixture of potassium ferricyanide and lead ferrocyanide in contact with a platinum electrode as an indicator for lead ions in the potentiometric titration of sulfate with lead nitrate. We have found that a ferricyanide–cerous potassium ferrocyanide mixture acts as a good indicator for cerous ions. The potential of a ferri–ferrocyanide mixture in contact with platinum at 25° is represented by

$$E = e_0 + 0.0591 \log \frac{[Fe(CN)_6^{\equiv}]}{[Fe(CN)_6^{--}]}$$

If the ferrocyanide ions are furnished only by a saturated solution of cerous potassium ferrocyanide, then for the saturated solution

$$[Ce^{+++}]\cdot[K^+]\cdot[Fe(CN)_6^{--}] = \textbf{Solubility product of } CeKFe(CN)_6$$

and

$$[Fe(CN)_6^{--}] = \frac{k}{[Ce^{+++}]\cdot[K^+]}$$

The potential of the electrode becomes

$$E = e_0 + 0.0591 \log \frac{[Fe(CN)_6^{\equiv}]\cdot[Ce^{+++}]\cdot[K^+]}{k}$$

and if $[Fe(CN)_6^{\equiv}]$ and $[K^+]$ are constant, dilution of the solution during titration being disregarded

$$E = e_0' + 0.0591 \log [Ce^{+++}]$$

The electrode potential is thus shown to be directly proportional to the logarithm of the molar concentration of the cerous ion. Actually such a

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(10) An extended treatment of the ferri–ferrocyanide electrode is given by Kolthoff and Furman "Potentiometric Titrations," second ed., John Wiley and Sons, New York, 1931, pp. 64–69 and 318–34.

(11) Tomiček, *Rec. trav. chim.*, 44, 410 (1925).

(12) Treadwell and Chervet, *Helv. Chim Acta.* 6, 550 (1923).

(13) Atanasiu, *J. chim. phys.*, 23, 501 (1926); *Compt. rend.*, 182, 519 (1926).

(14) Kolthoff and Furman, Ref. 10, pp. 66 and 331.

simple relation does not apply due to the dependence of the potential of the ferri–ferrocyanide electrode upon the salt concentration of the solution. For large quantities of fluoride or in the presence of large amounts of foreign salts no breaks in potential were obtained at the equivalence point.

Experimental

Apparatus and Materials.—The indicator electrode was a spiral of bright platinum wire and the reference electrode was a saturated calomel cell of the type recommended by Müller and by Kolthoff and Furman.[15] This cell was connected by a long salt bridge of saturated potassium nitrate with the solution to be titrated, a long bridge being necessary because all titrations were performed at 70". The potentiometer was a Leeds and Northrup Potentiometric Unit, No. 4908. Titrations were made in open beakers using motor stirring and holding the temperature to within 1° of 70° with a small Bunsen flame.

Standard solutions of sodium fluoride of normalities 0.1000, 0.0100 and 0.0050 were prepared by the method used by Hawley[16] and by Allen and Furman.[17] Various amounts were measured out from calibrated pipets.

The cerous nitrate used was a C. P. product which was recrystallized once from water. The cerium content of the solution prepared was determined by oxidizing measured portions to the ceric state with ammonium persulfate using silver nitrate as a catalyst[18] and titrating back with ferrous sulfate which had been checked against standard potassium permanganate. Other analyses were made by evaporating down definite volumes of the solution and igniting the residue to constant weight; the cerium content of the ignited residue was then determined as above. Such analyses gave an average of 97.82% ceric oxide in the residue. The original cerous nitrate contained as impurities nitrates of the other rare earths but as Batchelder and Meloche[19] have pointed out such impurities may be disregarded and the normality of the solution calculated from the weight of the ignited residue, assuming it to be pure ceric oxide. In the present case this method was used since the other rare earth nitrates would change the normality of the solution to fluorine only by about 0.1%.

The potassium ferricyanide was used as an approximately 0.1 molar solution of a C. P. salt free from ferrocyanide. The cerous potassium ferrocyanide was precipitated by mixing equivalent volumes of cerous nitrate and potassium ferrocyanide and the precipitate was washed repeatedly with distilled water by decantation. This substance was used as a suspension in water. It is possible that the precipitate contained some $Ce_4[Fe(CN)_6]_3$, but this would not affect the results in any way.

Outline of the Method.—Some preliminary work had shown that cerous fluoride was precipitated in a gelatinous state and that it adsorbed excess cerous ions to a high degree; no gravimetric determination of fluorine as cerous fluoride could be made. This finding checks the results of Batchelder and Meloche.[8] On the other hand, at 70° and in a solution containing 50% ethyl alcohol by volume good results were secured by the potentiometric titration method. Other temperatures were tried but 70° gave the best results. This is about the same temperature that Atanasiu[13] used in his work. In accordance with the experience of Kolthoff with the sulfate titration, steady potentials were obtained only with 50% alcohol, other concentrations gave erratic readings. The procedure for the titrations recorded in Table I follows. The volumes of sodium fluoride

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(15) Ref. 10, pp. 79–81.

(16) *Hawley, Ind Eng. Chem* , 18, 573 (1926)

(17) *Allen and Furman,* THIS JOURNAL, *64,* 4625 (1932).

(18) Willard *and Young, ibid., 60* ,1370 (1928).

(19) Ref. 8, p. 2132.

used were measured out by pipets and diluted with water and 95% ethyl alcohol so that the final volume contained 50% alcohol. The total volume of the solution titrated was 70–80 ml. for Titrations 1–22, 50 ml. for 23–34 and 25–30 ml. for 3544. Three to five drops of 0.1 *M* potassium ferricyanide (about 0.25 ml.) and about 10 mg. of the cerous potassium ferrocyanide suspension were then added. The exact amount of the ferrocyanide used may vary somewhat but it should be cut down for the smaller quantities of fluorine. The amount of ferricyanide must be kept fairly constant at the value given. The solution was then heated to 70° and the titration performed at that temperature, not deviating more than one degree. With a 50-ml. buret, volume increments of 0.05 ml. were used near the equivalence point and with the micro-buret the increment was 0.02 ml. The equivalence point was located by computing the difference quotients in the usual manner. With volume increments of 0.05 ml. the break in potential at the equivalence point ranged from about 20 millivolts for the larger amounts of fluorine to about 90 mv. for the smaller quantities. Volume increments of 0.02 ml. used in the case of the micro-buret gave breaks of 30-40 millivolts. The potential curve for Titration No. 40 is given in Fig. 1, and is typical of the course of the potential during every titration.

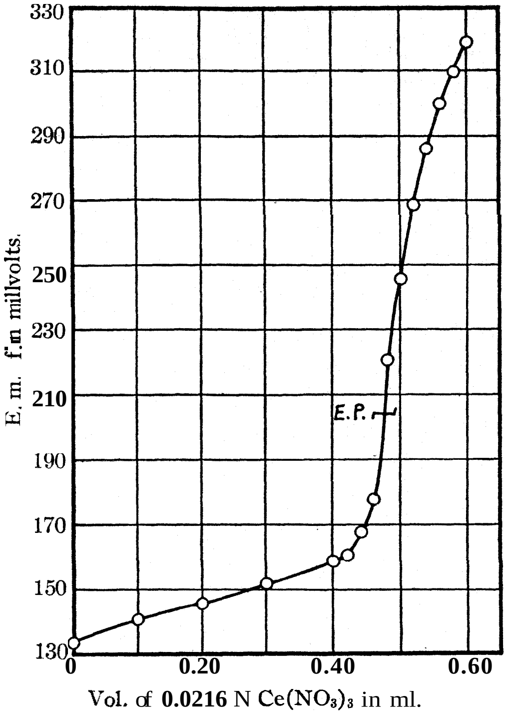

Fig. 1.—Titration of 0.19 mg. of fluorine with 0.0216 *N* cerous nitrate.

TABLE I

TITRATION OF FLUORIDE WITH CEROUS NITRATE SOLUTION

A. Using 50-ml. buret

Nos.	NaF, ml.	F pres., mg.	Mean vol. $Ce(NO_3)_3$, ml.	N of soln.	Mean wt. of F found, mg.	Deviation from correct wt. F Av., mg.	Deviation from correct wt. F Max., mg.
1–6	24.98	47.46	25.19	0.0992	47.48	±0.07	−0.17
7–11	9.96	18.92	10.02	.0992	18.89	− .03	− .05
12–17	4.99	9.48	5.08	.0992	9.57	± .09	+ .15
18–22	2.02	3.84	2.01	.0992	3.79	− .04	− .09
23–28	9.96	1.89	2.00	.0500	1.90	± .01	+ .04

B. Using micro-buret

Nos.	NaF, ml.	F pres., mg.	Mean vol. $Ce(NO_3)_3$, ml.	N of soln.	Mean wt. of F found, mg.	Deviation from correct wt. F Av., mg.	Deviation from correct wt. F Max., mg.
29	10.06	0.96	0.464	0.1080	0.95	−0.01	−0.01
30–34	9.96	.95	0.994	.0500	.95	± .00	− .02
35–39	4.99	.47	1.200	.0216	.49	+ .02	+ .03
40–44	2.02	.19	0.476	.0216	.20	+ .01	+ .01

Discussion of Results.—The amount of fluorine that may be titrated by the method ranges from about 0.1 mg. to 50 mg. With a quantity greater than this upper value no break in potential is observed. This is undoubtedly due to the effect of a high salt concentration on the ferri–ferrocyanide potential, but the volume of the solution must not be too large as the method is a precipitation titration and depends on the separation of the cerous fluoride. 0.1 mg. is the lower limit set by the volumes that must be taken. In order to titrate an amount of fluorine smaller than this a more dilute solution of cerous nitrate would have to be used and then the dilution would be so great that the break in potential would not be observed at the equivalence point.

Cerous fluoride is less soluble than cerous potassium ferrocyanide so with large amounts of fluorine all of the ferrocyanide goes into solution as shown by the equation

$$3F^- + CeKFe(CN)_6 \longrightarrow CeF_3 + K^+ + Fe(CN)_6^{---}$$

As cerous nitrate is run in the excess fluoride is first precipitated and when this reaction is completed the ferrocyanide begins to reprecipitate. There is of course no indication of the completion of the cerous fluoride precipitation but since an amount of cerium equivalent to the fluoride precipitated in the beginning will be required for the ferrocyanide the correct equivalence point is shown by the break in the ferri–ferrocyanide potential. With small amounts of fluorine perhaps all of it is precipitated and the method then becomes simply a titration of ferrocyanide with cerous cerium.

The gelatinous nature of cerous fluoride and the presence of cerous potassium ferrocyanide cause poisoning of the platinum electrode. After several titrations the electrode responds very sluggishly and the magnitude of the potential breaks decreases rapidly, hence the electrode must be cleaned often by standing in cleaning solution, then washing with distilled water and igniting.

Interfering Substances.—Ions which give precipitates with cerous cerium must be absent, thus excluding hydroxide, carbonate, phosphate, etc. The solution cannot be acid, as the cerous potassium ferrocyanide is readily soluble in dilute acids. Large amounts of salts completely obscure the potential break but with only small amounts present the titration may be performed. In some experiments with 19 mg. of fluorine good results were secured in the presence of 0.5 g. of sodium chloride. Successful titrations were also made in the presence of 0.5 g, of potassium chloride, of sodium nitrate and potassium nitrate; 0.5 g. of sodium sulfate, however, completely obscured the potential break; in the presence of about 0.2 g. the determination could be made. The breaks in potential with solutions containing foreign salts are not as large as with solutions of pure fluorides. A solution of sodium fluoride containing 19 mg. of fluorine and 50 mg. of sodium silicate and another one with 32 mg. of sodium borate were neutral-

:ed to phenolphthalein and titrated. Potential breaks were secured but hey came at too large a volume of cerous nitrate.

The method was applied to the determination of the percentage of uorine in the Bureau of Standards sample of fluorspar, No. 79. The uorine was extracted by the Berzelius method using a double fusion as utlined In a previous paper.[17] Since the titration works well only with mall amounts of fluorine and foreign salts must be present in small concentrations, it was necessary to resort to the use of aliquot parts of the preared solutions of fluoride. The analyses are recorded in Table II.

TABLE II

DETERMINATION OF FLUORINE IN FLUORSPAR

Using micro-buret, $Ce(NO_3)_3$ 0.1080 *N*

Sample, g.	Tot. vol., ml.	Vol. for titr., ml.	Vol. $Ce(NO_3)_3$ A	B	C	% F A	B	C	Av. % F
0.2427	249.92	10.06	2.244	2.234	2.224	47.13	46.92	46.71	46.92
.3075	249.92	10.06	2.796	2.816		46.35	46.68		46.52
.3648	249.85	10.06	3.309	3.319	3.299	46.23	46.37	46.09	46.23

Average of all titrations, 46.56%. Bureau of Standards value, 46.20%.

The potential breaks at the end-points ranged from 15 to 25 millivolts for .02 ml. of reagent. The results run slightly high; this may be due to the oreign salts present or to a slight amount of carbonate which might not lave been removed. Considering the small samples involved in the taking f aliquots and the relatively high concentrations of sodium and potassium itrates in the solutions, the results exhibit a fair degree of accuracy.

Acknowledgment.—This work was done with the aid of a fellowship grant in analytical chemistry from the J. T. Baker Chemical Company of Phillipsburg, New Jersey. Gratitude is here expressed for this support.

Summary

A potentiometric titration method for fluorine involving the precipitation of cerous fluoride has been developed through a new application of the ferri–ferrocyanide electrode.

The method gives good results for amounts of fluorine ranging from 0.1 mg. to 50 mg. Small amounts of foreign salts may be present but large amounts mask the equivalence point. Ions which precipitate cerous cerium must be absent. Fluorspar has been analyzed by the method.

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The Temperature Coefficient of the Photosensitized Hydrogen–Oxygen Reaction

BY HUGH S. TAYLOR AND DONOVAN J. SALLEY

The mechanism of the hydrogen–oxygen reaction at high temperatures has been the subject of considerable discussion recently. All of th schemes postulated for the reaction involve a chain, with either excite molecules or free atoms and radicals as propagating agents. One of th general characteristics of a chain reaction is that there exists a temperature region in which its reaction velocity does not obey the Arrheniu equation d ln $k/dT = E/RT^2$, but increases more rapidly with temperature than this law demands. Such a reaction is said to possess an ant Arrhenius temperature coefficient. This behavior arises from the fac that there will be superposed on the ordinary temperature effect, whic causes an increase in the number of reactions initiated, an additiona temperature effect due to increase in the length of each chain starte As a result of these two influences, the change of reaction velocity wit temperature cannot be expressed by a simple law.

The temperature coefficient of the direct photochemical hydrogen oxygen reaction has been measured by Andrejeff[1] and by Coehn an Grote[2] These investigators found that the value of k_{t+10}/k_t was onl 1.04–1.06 in the range 130–240°. Consequently, increase in temperatur did not result in marked increase in chain length in this temperature range Kistiakowsky[3] showed for the same reaction that, whereas the temperature coefficient was 1.05 at room temperatures, it increased to 1.25 a temperatures above 500°. Kistiakowsky concluded that over a considerable temperature range only short chains existed, but that above 500°, quite long chains were propagated in the illuminated gas mixture

More recently Farkas, Haber and Harteck[4,5] have determined the chain lengths in hydrogen–oxygen mixtures sensitized to light by ammonia Their work indicated that water formation proceeded by a chain, the length of which increased exponentially with temperature, as expressed by the empirical equation $l_t = 3\,e^{0.023(t-200)}$, where l_t is the chain length at the temperature t°C.[5] This gives at about 400° a chain of about 350 molecules of water for each hydrogen atom produced by light from the ammonia. Furthermore, explosions occurred at temperatures about 420' and oxygen–hydrogen pressures above 300 mm. These results would

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[1] Andrejeff, *J. Russ. Phys.-Chem. Soc.*, *43*, 1345 (1911).

[2] Coehn and Grote, Nernst-Festschrift, 1912.

[3] Kistiakowsky, *Proc. Nat. Acad. Sci.*, *15*, 194 (1929).

[4] Farkas, Haber and Harteck, *Naturwissenschaften*, **18**, 266 (1930); *Z. Elektrochem.*, 36, 711 (1930).

[5] Haber, *Naturwissenschaften*, **18**, 917 (1930).

indicate that the chains were lengthening rapidly as the temperature increased, becoming very long at comparatively low temperatures. To explain their findings, these authors used the Bonhoeffer–Haber mechanism of water formation,[4,5,6,7] which postulates chain propagation by means of hydrogen atoms and hydroxyl radicals. To explain the explosions, it was suggested in addition that chain branching could occur through a reaction producing two hydroxyl radicals.

Now, the results obtained in ammonia–hydrogen–oxygen mixtures are at variance with those of the direct photochemical reaction as measured by Kistiakowsky. The initial difference between the two reactions would seem to lie in the fact that following light absorption, hydrogen atoms are produced in the former whereas oxygen atoms are formed in the latter. The oxygen atoms must, however, react with the hydrogen by the step[8]

$$O + H_2 = OH + H \qquad (1)$$

Although reaction step (1) has a small activation energy, it should be completely efficient at about 400°. Therefore, if the Haber mechanism bc correct, both the OH radical and the H atom could initiate a chain. Consequently, it is to be expected that chain lengths in both the direct photochemical and the ammonia sensitized reaction should be about the same at comparable temperatures. This does not appear to be the case.

Hydrogen atoms can be produced at high temperatures from the action of excited mercury on molecular hydrogen. At ordinary temperatures, Marshall[9] has determined the chain length in the mercury sensitized hydrogen–oxygen reaction, finding an average value of 2.5 molecules per quantum. He also determined the temperature coefficient of the reaction to be 1.04 over a limited temperature range. In view of the discrepancy of the direct photochemical and the ammonia sensitized hydrogen–oxygen reaction, and because of the suitable character of the mercury sensitized reaction, a comparison of the temperature coefficients of the mercury sensitized and the ammonia sensitized reactions is of importance. The anti-Arrhenius behavior of the temperature coefficients should indicate the temperature at which long chains are set up in the reaction mixtures.

The Mercury Sensitized Reaction.—The experiments on the mercury sensitized hydrogen–oxygen reaction were carried out in a circulatory system, in order that the gases could be kept saturated with the mercury contained in a glass spiral saturator. The reaction vessel proper was of quartz, 10 cm. long, 1.8 cm. diameter, and 0.5 mm. wall thickness. It was kept at the desired temperatures by an electric furnace. The source of illumination was a water cooled Cooper–Hewitt mercury arc.

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[6] Bonhoeffer and Haber, *Z. physik. Chem.*, 137A, 363 (1928).

[7] Haber, *Z. angew. Chem.*, 42, 475 (1929).

[8] Kistiakowsky, THIS JOURNAL, 52, 1868 (1930).

[9] Marshall, *J. Phys. Chem.*, 30, 34 (1926); 30, 1078 (1926); THIS JOURNAL, 54, 4460 (1932).

Starting in every case with a 2:1 $H_2:O_2$ mixture at 600 mm. total pressure, reaction rates were measured at various temperatures from 280 to 535°, and with mercury pressures of 0.0004, 0.0035, and 0.020 mm. Each individual reaction showed an induction period of one or two minutes, but thereafter progressed at a constant speed, measured by the slope of the straight line portion of the time–dp curves. In order to check the temperature coefficient from time to time, the light intensity of one series

TABLE I

DEPENDENCE OF RATE ON TEMPERATURE

Initial pressure 600 mm. P_{Hg}, 0.0004 mm. Ratio $H_2:O_2$, 2:1

No.	Temp.	dp/dt mm./10 min.	I/I_0	dx/dt
D1	356	3.0	0.166	18.1
D2	451	5.0	.166	30.1
D3	506	7.5	.166	45.2
D4	534	69.5	.166	418.8
H1	289	5.4	.562	9.0
H2	349	9.0	.562	16.0
H3	451	20.5	.562	36.5
H4	506	31.0	.562	55.1
H5	534	108.0	.562	191.9
I1	290	15.0	1.00	15.0
I2	348	17.5	1.00	17.5
I3	405	26.5	1.00	26.5
I4	454	33.5	1.00	33.5
I5	505	47.5	1.00	47.5
I6	534	95.0	1.00	95.0
			P_{Hg}, 0.0035 mm.	
B1	270	8.2	0.860	9.5
B2	404	22.2	.860	25.7
B3	454	27.7	.860	32.2
B4	508	33.5	.860	39.0
A1	271	8.2	.803	10.2
A2	361	16.2	.803	20.2
A3	377	18.3	.803	22.8
A4	403	19.5	.803	24.3
A5	432	21.0	.803	26.2
C1	316	8.5	.595	14.3
C2	345	10.1	.595	17.0
C3	406	15.0	.595	25.2
C4	452	19.0	.595	31.9
C5	506	28.0	.595	47.1
E1	280	13.0	1.00	13.0
E2	347	17.7	1.00	17.7
E3	404	23.0	1.00	23.0
E4	451	32.5	1.00	32.5
E5	507	57.5	1.00	57.5
E6	534	118.6	1.00	118.5

TABLE I (*Concluded*)

No.	Temp.	dp/dt mm./10 min.	P_{Hg}, 0.020 mm I/I_0	dx/dt
G1	287	20.0	1.00	20.0
G2	350	24.0	1.00	24.0
G3	404	31.5	1.00	31.5
G4	452	35.5	1.00	35.5
G5	507	59.5	1.00	59.5
G6	534	112.5	1.00	112.5
J1	235	6.0	0.427	14.1
J2	302	9.0	.427	21.1
J3	360	12.0	.427	28.1
K1	230	8.0	.668	12.0
K2	400	20.0	.668	30.6
K3	440	25.2	.668	37.7
K4	442	25.0	.668	37.4
K5	510	37.0	.668	55.3
K6	512	35.0	.668	52.4
F1	279	9.0	.536	16.8
F2	337	13.0	.536	24.3

of runs was taken as a standard, and other series (made with the same mercury pressure) were correlated with this standard.

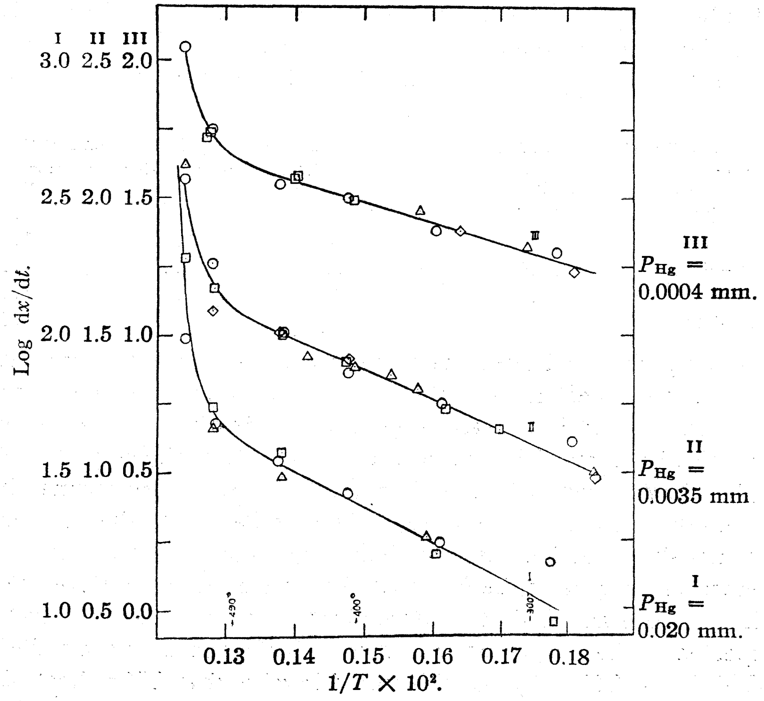

Fig. 1.—Variation of log dx/dt with $1/T$.

A reaction in the dark appeared at temperatures above 490° and amounted in some instances to as much as 25% of the total rate with light. The dark reaction velocity was subtracted from the total velocity in order to obtain the true light velocity.

The data are summarized in Table I, and represented graphically on a log dx/dt–$1/T$ plot, Fig. 1. (The figures under dx/dt were obtained by dividing the values under dp/dt by the ratio I/I_0.)

Discussion

A study of the data presented in the table and the figure reveals the fact that the temperature coefficient of the mercury sensitized hydrogen–oxygen reaction is anti-Arrhenius in character only above 490°. At lower temperatures, the temperature coefficient is small, and follows the Arrhenius law more or less closely. The value of the "constant" E of the Arrhenius equation, calculated from the slope of the curves of Fig. 1, increases from about 3000–5000 calories in the low temperature range to greater than 25,000 calories at high temperatures. The conclusion can, therefore, be drawn that below 490°, the length of the reaction chains does not change sensibly, but that at higher temperatures, the length of the chains increases very rapidly with increasing temperature.

This same conclusion was reached by Kistiakowsky[3] in regard to the direct photochemical reaction. For purposes of comparison with his results, the averaged temperature coefficients, k_{t+10}/k_t have been calculated for the photo-sensitized reaction, and are tabulated in Table II

TABLE II

TEMPERATURE COEFFICIENT OF HYDROGEN–OXYGEN PHOTOREACTION

Temperature interval, °C.	Photochem. reaction	Mercury photosensitized reaction P_{Hg}, 0.0004	0.0035	0.020
300–400	1.07	1.12	1.09	1.05
400–490	1.13	1.08	1.07	1.05
490–505	1.25	..	..	..
490–510	..	1.17	1.14	1.13
510–530	..	1.37	1.39	1.31

This comparison indicates that a very close agreement exists between the temperature coefficients of the photochemical and the mercury sensitized reactions, and it is reasonable to conclude that the two reactions are practically identical in this respect. Now, Kistiakowsky[3] has shown that the chains produced in both reactions were of approximately the same length at room temperatures. The similarity of the temperature coefficients shows further that the chain lengths are about the same at all temperatures, in spite of the fact that the oxygen atoms initiate the reaction in one case and hydrogen atoms in the other. Such a result is to be expected if the oxygen atoms produce hydrogen atoms by the reaction $O + H_2 = OH + H$, and this would involve that OH radicals do not participate in the chain at least below 490°.

It appears from these results that the mercury sensitized hydrogen–oxygen reaction does not show the characteristics reported by Farkas, Haber and Harteck for the ammonia sensitized reaction. In order to make a direct comparison of the two reactions, a study of the ammonia sensitized reaction was undertaken, using the same apparatus as described above for the mercury sensitized reaction.

The Ammonia Sensitized Reaction.—The ammonia used in the experiments on the ammonia sensitized hydrogen–oxygen reaction was supplied by solutions of ammonium hydroxide contained in a small efficient bubbler cooled in an ice-bath. This method of supplying the ammonia insured a constant partial pressure of both ammonia and water vapor during a run. The source of illumination was a Cooper Hewitt mercury arc, operated as a hot arc on 8 amperes and 80 volts.

Before presenting the main results and general discussion, one or two observations of interest should be reported.

The **Dark** Reaction.—When the experiments in this investigation were first commenced, no dark reaction was observable before illumination of the reaction mixture. However, after some fifty separate runs, a slow dark reaction could be detected preceding the light reaction, even at temperatures as low as 300°. When no experiments had been made for several days, on recommencing the runs this dark reaction would not appear for the first few experiments, but, thereafter, would be noticeable in the fresh gas mixtures.

A dark reaction was always observed after every light reaction. For the first minute or two after cutting off the light, the rate of this dark reaction was about 50% of the light rate, but then fell to a very small value. That a dark reaction persisted for a considerable time, however, was shown by permitting a mixture, in which reaction had been initiated previously by light, to stand for several hours in the dark. During this interval a pressure decrease occurred.

The Effect of Mercury.—Since mercury served as the valves and piston of the circulating pump, no attempt was made to remove the mercury vapor from the gases for these experiments with ammonia as a sensitizer. That no sensitization by mercury was taking place was shown by the fact that no reaction occurred in the absence of ammonia when the arc was operated hot. Moreover, the rate of the ammonia sensitized reaction was not affected by varying the partial pressures of mercury from 0.0004 to 0.020 mm. Although this determination was made only for the one partial pressure of ammonia of 14.5 mm., it has been assumed that the presence of mercury has no effect on the reaction rates at other ammonia concentrations.

The Effect of Temperature and of Ammonia Pressure.—Reaction rates for ammonia–oxygen–hydrogen mixtures sensitized to light were measured over a temperature range from 275–450°, and with partial pressure of ammonia from 1.3 mm. up to 97.5 mm. In every case the partial pressures of hydrogen and of oxygen in the system were 400 mm. and 200 mm., respectively. The pressure of water was at all times less than 5 mm.

The graph of an individual reaction indicated that an induction period of one or two minutes existed, after which the reaction proceeded smoothly at a constant speed, measurable by the slope of the straight line portion of the time–d*p* curve. The reaction rates were quite reproducible, checking within ±4%. Every effort was made to keep the light intensity and other conditions constant during the whole series of experiments, in order that the rates measured at various pressures of ammonia and at various temperatures could be compared directly. That constancy of conditions actually prevailed over a long time was indicated by checking the runs at a given partial pressure of ammonia (14.4 mm.) at intervals during the investigation. The complete data are collected in Table III, showing the reaction rate observed at each temperature and ammonia pressure. Most of the rate values recorded are the mean of two or more duplicate runs. (The values listed under d*x*/d*t* were obtained by dividing the figures under d*p*/d*t* by the ratio of 1/10.)

TABLE III

DEPENDENCE OF RATE ON TEMPERATURE AND ON AMMONIA CONCENTRATION

Series Letter	NH_3, mm.	Temp., °C.	$-dp/dt$ mm./10 min.	I/I_0	dx/dt
N	1.3	317	2.0	1.00	2.0
		381	1.1	1.00	1.0
		404	3.0	1.00	3.0
		433	2.0	1.00	2.0
		452	6.5	1.00	6.5
K	2.5	272	2.4	1.00	2.4
		324	2.5	1.00	2.5
		355	3.0	1.00	3.0
		381	6.8	1.00	6.8
		404	21.2	1.00	21.2
		422	192.5	1.00	192.5
		433	203.0	1.00	203.0
		435	237.5	1.00	237.5
S	4.8	276	11.9	1.335	8.9
		317	25.5	1.335	19.1
		352	70.5	1.335	52.9
		379	119.0	1.335	89.0
		404	180.0	1.335	134.9
		430	231.0	1.335	173.0
J	5.6	271	6.0[a]	1.00	6.0
		355	70.0	1.00	70.0
		378	95.5	1.00	95.5
		404	151.0	1.00	151.0

TABLE III *(Concluded)*

Series letter	NH_3, mm.	Temp., °C.	$-dp/dt$ mm./10 min.	I/I_0	dx/dt
R	8.9	277	37.0	1.335	27.7
		314	55.7	1.335	41.5
		350	77.5	1.335	58.0
		380	112.5	1.335	84.3
		403	151.5	1.335	113.0
		424	192.0	1.335	144.2
		430	228.0	1.335	170.8
L	9.6	272	6.2[a]	1.00	6.2
		355	55.8	1.00	55.8
		378	83.0	1.00	83.0
		404	122.3	1.00	122.3
T	9.6	275	26.3	1.335	19.6
		314	57.3	1.335	42.9
		351	77.3	1.335	58.3
		380	106.0	1.335	79.4
		404	150.0	1.335	112.4
	14.5	200	8.0	1.00	8.0
		271	24.3	1.00	24.3
		324	41.0	1.00	41.0
		351	54.0	1.00	54.0
		376	79.0	1.00	79.0
		404	107.7	1.00	107.7
		422	136.0	1.00	136.0
		440	169.5	1.00	169.5
M	31.5	272	13.5	1.00	13.5
		355	38.5	1.00	38.5
		381	57.5	1.00	57.5
		404	83.5	1.00	83.5
I	97.5	271	8.3	1.00	8.3
		355	16.2	1.00	16.2
		378	23.0	1.00	23.0
		404	34.4	1.00	34.4

[a] These abnormally low values for which we have no explanation have been omitted in the graphical representation and in the conclusions drawn from these latter.

The Temperature Coefficient.—A plot of the data of Table III on a log dx/dt–$1/T$ graph, Fig. 2, shows that the reaction velocity of the ammonia sensitized hydrogen–oxygen reaction increases *from 300° upward* more rapidly with temperature than the Arrhenius equation requires. Although this effect is observed with all concentrations of the sensitizer, it is more pronounced when lower partial pressures are employed. The curve obtained with 2.5 mm. of ammonia is particularly striking in this respect.

No explosions were obtained at temperatures up to 435–440°, although the reaction rate was becoming so fast at these temperatures that it seemed likely that explosions might have occurred a few degrees higher.

The Effect of Ammonia Concentration.—The dependence of reaction rate on the concentration of ammonia is indicated in Fig. 3, in which dx/dt is plotted against the partial pressure of ammonia, at three different temperatures. The rate values used in constructing this graph were those read off for the desired temperatures from a graph of the temperature coefficients plotted from all the data of Table III.

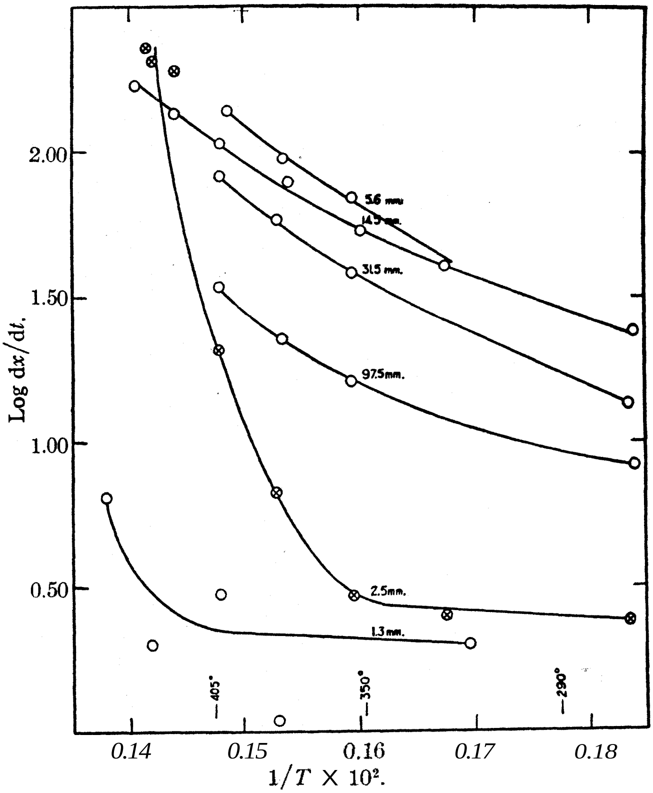

Fig. 2.—Variation of log dx/dt with $1/T$.

The curves indicate the remarkable dependence of reaction rate on the ammonia concentration. For any given temperature, there exists a concentration of ammonia at which the reaction rate is a maximum. The interpretation of this fact is that at concentrations of ammonia less than that required to give the maximum rate, the chain propagating influence of ammonia is effective, while at concentrations greater than the optimum, a chain breaking effect of ammonia becomes predominant.

The Chain Length.—In order to estimate the length of the chains occurring in the reaction, the rate of photodecomposition of ammonia was measured. Since this reaction is slow, and since the total volume of the system used for the ammonia sensitized hydrogen-oxygen reaction was large (280 cc.), a direct determination of the ammonia decomposition rate by following pressure change could not be made in that apparatus. Therefore, using the same reaction vessel and furnace, a small static system of total volume of 48 cc. was constructed in which to measure ammonia decomposition. The arrangement of arc, furnace and reaction vessel was the same in this apparatus as in the ammonia sensitized reaction, so that the conditions under which reaction took place were comparable in both cases. The same arc, operating at the identical voltage and amperage, was employed. Tank ammonia, purified by fractional distillation at low temperatures, was used in these experiments.

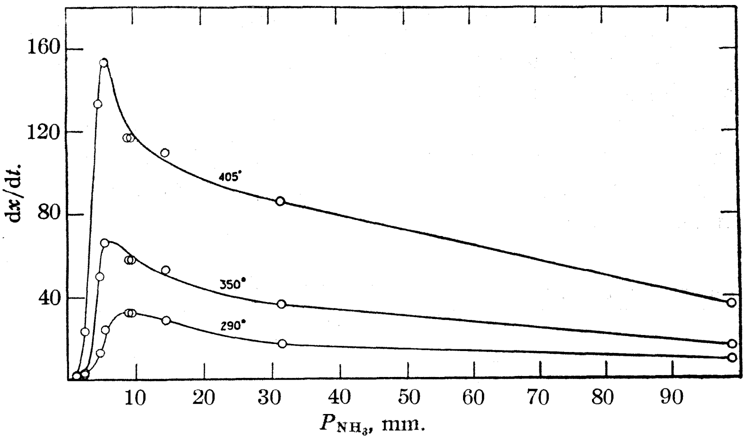

Fig. 3.—Dependence of reaction rate on ammonia pressure.

The rate of the photodecomposition was measured at temperatures from 300 to 450°, and at ammonia pressures from 10 to 100 mm. by following the pressure increase with a constant volume mercury manometer. It was found that the reaction rate fell off as the reaction progressed; consequently the pressure increase occurring in the first two minutes was taken as a measure of the rate of reaction. Also, practically no temperature coefficient was observed for the photodecomposition rate.[10] Consequently, in obtaining the dependence of rate on initial ammonia concentration, the rates observed at the several temperatures were all plotted against the pressure of ammonia. The smooth average curve drawn through all the combined data was of the form $dx/dt \propto I_{abs} = (1 - e^{-\alpha[NH_3]})$, indicating that the decomposition rate was directly proportional to the ammonia pressure in the low concentration range, and independent of the ammonia pressure at higher concentrations. Complete

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[10] *See* Wiig and Kistiakowsky, THIS JOURNAL, 54, 1805 (1932). They find but a slight increase in quantum yield with temperature from 300 to 500°, contrary to Kuhn. *Compt.* rend.. 178, 708 (1924)

absorption was achieved only at fairly high pressures of ammonia, for we were probably dealing only with the weak 2260 Å. ammonia absorption band.

A calculation was then made of the number of moles of ammonia decomposed in unit time in the photodecomposition of ammonia, and compared with the number of moles of water produced in the ammonia sensitized hydrogen-oxygen reaction. The ratio moles of water formed in unit time to moles of ammonia decomposed in unit time should be a measure of the length of the chain existing in the hydrogen–oxygen mixture at a given temperature, assuming that only the hydrogen atoms produced by light from the ammonia are effective in starting chains.[11]

The final figures are collected in Table IV. The first column gives the pressure of ammonia; the second the average number of moles of ammonia decomposed in unit time at any temperature from 290 to 430°; the third, the number of moles of water formed in unit time at 290° in the ammonia sensitized reaction; and the fourth, the ratio of the moles of water formed to the moles of ammonia decomposed. The remaining columns of the table give the corresponding data for the temperatures of 350 and 405°, respectively.

TABLE IV

THE DEPENDENCE OF THE RATIO $\Delta nH_2O/\Delta nNH_3$ ON TEMPERATURE AND AMMONIA CONCENTRATION

		290°		350°		405°	
p_{NH_3}	Av. moles NH_3 decomp. per min. × 10^7	Moles H_2O formed per min. X 10^7	Ratio $\frac{\Delta nH_2O}{\Delta nNH_3}$	Moles H_2O formed per min. X 10^7	Ratio $\frac{\Delta nH_2O}{\Delta nNH_3}$	Moles H_2O formed per min. X 10^7	Ratio $\frac{\Delta nH_2O}{\Delta nNH_3}$
1.3	0.7	...	..	18	25	17	26
2.5	1.3	22	16	24	19	214	115
4.8	2.6	116	47	431	175	1144	460
5.6	2.8	217	76	575	200	1303	504
8.9	4.7	284	59	500	100	1003	210
9.6	5.2	284	55	500	96	1003	194
14.5	7.7	253	33	474	63	876	123
31.5	15.0	151	10	310	21	732	49
97.5	24.1	796	3	205	6	294	13

Discussion

A comparison of the results of our experiments on the mercury sensitized and the ammonia sensitized hydrogen–oxygen reactions indicates that the temperature coefficients of the two do not behave in the same manner, but are in fact quite divergent. However, our findings on the temperature sensitivity of ammonia–hydrogen–oxygen mixtures are essen-

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[11] If the true quantum yield of the ammonia photodecomposition at these temperatures is 0.5, as reported by Kistiakowsky and Wiig, the true chain lengths in the ammonia sensitized reaction should be just one-half of the values reported for the ratio moles water formed to moles ammonia decomposed.

tially in agreement with those of Farkas, Haber and Harteck. This is shown by the following comparative data.

	Farkas, Haber and Harteck	Present work
Total pressure, mm.	500	600
Ratio, $H_2:O_2$	2:1	2:1
Pressure of NH_3, mm.	3	2.5
Molecules water formed per second at 290°	$a \times 10^{17}$	5.5×10^{15}
Molecules water formed per second at 405°	2.5×10^{18}	4.5×10^{16}
Ratio $\dfrac{\text{Molecules per sec. at } 405°}{\text{Molecules per sec. at } 290°}$	8.3	8.2

Our Table IV indicates that the so-called "chain length" is not constant at a given temperature, as it should be, but varies with the concentration of the sensitizer. This is very clearly brought out in Fig. 4, where the ratio moles water formed to moles ammonia decomposed, is plotted against the ammonia pressure. On the low pressure side of the maximum the ratio is dependent almost exactly on the square of the ammonia pressure, while on the high pressure side, the values are inversely proportional to the 1.3 power of the ammonia pressure. The fact that the "chain length" is not constant even at the lower pressures of ammonia, where its inhibiting effect does not enter, indicates the strong influence of the ammonia on the course of the reaction.

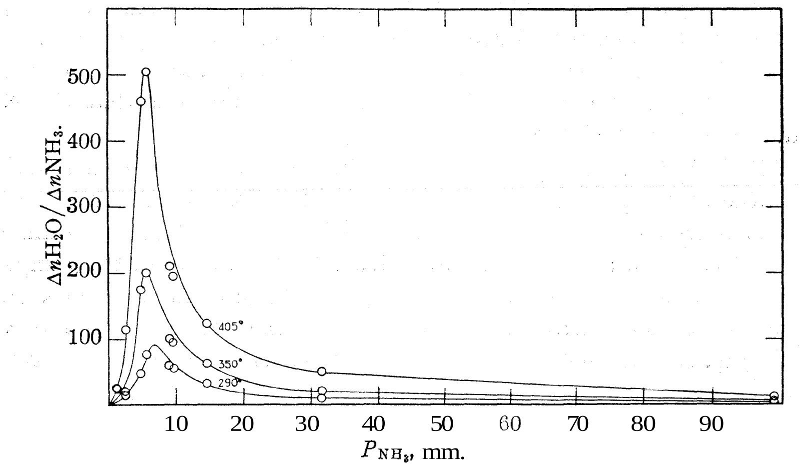

Fig. 4.—Dependence of the ratio, moles of water formed to moles of ammonia decomposed, on the ammonia pressure.

From the facts brought out above, it seems clear that sensitization of hydrogen-oxygen mixtures by ammonia is not simply a case of initiation of reaction by hydrogen atoms. On the contrary, the reaction mechanism must be much more complicated. We suggest as possibilities that NH_2 radicals, and intermediate oxidation products of these, are helping to propagate long chains. It was pointed out some time ago[12] that with oxygen as one of the reactants in the system, there is always the possibility that primary interaction of oxygen with ammonia might influence the course of any reaction in which ammonia was used as a sensitizer. In work with other sensitizers, hydrogen sulfide, hydrogen bromide, etc., for the hydrogen–oxygen reaction, Farkas, Haber and Harteck[13] find that the sensitizer not only produces hydrogen atoms but also enters into oxidation reactions. In preliminary experiments on the photochemical oxidation of ammonia, we find that the rate of removal of ammonia when oxygen is present is three or four times as fast as the photochemical decomposition of ammonia under the same conditions when oxygen is absent. This implies that the photochemical oxidation of ammonia is a chain reaction which may be involved in the mechanism of the ammonia sensitized hydrogen-oxygen reaction. It is known that nitrogen dioxide has an enormous accelerating influence on the explosibility of hydrogen–oxygen mixtures, but evidence indicates that its action may be due to a wall effect. While the possibility of its intervention in the ammonia sensitized reaction cannot be excluded, we incline to the view that the NH_2 fragments are primarily responsible.

As the result of the investigation of the ammonia sensitized reaction, the source of the divergence between it and the mercury sensitized reaction has been located. The appearance of long chains in the ammonia sensitized reaction at temperatures at least 100° lower than the temperature at which they appear in the mercury sensitized or direct photochemical reaction is accounted for by the fact that the ammonia itself powerfully influences the course of the reaction, whereas the mercury has no similar effect.

Since, as is apparent from the preceding considerations, the ammonia and its decomposition products are important factors in determining the length of chain at a given temperature, it is evident that the results obtained from the sensitization experiments with ammonia cannot be used to determine the efficiencies of postulated reactions in the hydrogen–oxygen reaction chain. This has been done by Frankenburger and Klinkhardt, who used the chain length in the ammonia sensitized reaction as a function of temperature as a measure of the activation energy of the reaction $OH + H_2 = H_2O + H$. Had this been correct, the mercury sensitized reaction would have shown a similar temperature variation in the same temperature range. No such is observed. Furthermore, the ammonia concentration markedly affects the temperature variation. No significance attaches, therefore, to the value of 12,000 calories deduced thus for the activation energy, and the arguments based by Frankenburger and Klink-

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[12] Taylor and Emeleus. THIS JOURNAL, 53, 562 (1931).

[13] Farkas, Haber and Harteck, *Naturwissenschaften*, 18, 443 (1930).

hardt on this value are correspondingly weakened. This conclusion has been independently reached by Haber and Oppenheimer,[14] who note marked differences between the ammonia sensitized reaction and that initiated by atomic hydrogen from a tungsten arc. While we agree with their conclusion, we believe that their observations with the tungsten arc must be similarly suspect since they show abnormal sensitivity with temperature when compared with our mercury-sensitized and the photochemical reaction. We suspect a reaction accelerated by tungsten dust from the atomic hydrogen arc as the cause of Haber and Oppenheimer's results.

Summary

1. The temperature coefficients of the mercury sensitized and the ammonia sensitized hydrogen–oxygen reactions have been measured at high temperatures.

2. The temperature coefficient of the ammonia sensitized reaction is anti-Arrhenius at temperatures above 300° while that of the mercury sensitized reaction is anti-Arrhenius only above 490°, indicating that a marked increase in chain length occurs at a much lower temperature in the case of ammonia–hydrogen–oxygen mixtures.

3. The temperature coefficients of the mercury sensitized and the direct photochemical reactions of hydrogen and oxygen are shown to be comparable over the whole temperature range. It is suggested that the chain mechanism of the reaction is the same whether initiated by atomic oxygen or atomic hydrogen.

4. The rate of reaction in mixtures of hydrogen and oxygen sensitized by ammonia is markedly dependent on the concentration of ammonia. At low concentrations, a chain propagating influence of ammonia is effective; at high concentrations, a chain breaking effect of ammonia becomes predominant.

5. Sensitization of hydrogen–oxygen mixtures by ammonia is not simply a case of initiation of reaction by hydrogen atoms. It is suggested that NH_2 radicals and intermediate oxidation products of these help to propagate the chains.

6. The cause of the divergence of the ammonia sensitized from the mercury sensitized reaction of hydrogen and oxygen is ascribed to the powerful influence of ammonia on the course of the reaction.

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[14] Haber and Oppenheimer, Z. *physik. Chem.*, 16B, 443 (1932).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Production of Hydrogen Peroxide in the Mercury Sensitized Hydrogen–Oxygen Reaction

BY J. R. BATES AND D. J. SALLEY

In spite of a large number of investigations there still seems to exist considerable doubt as to the mechanism whereby oxygen reacts with hydrogen atoms produced by different methods.[1] Still more striking is the fact that there is no agreement among the various workers as to the primary products of the reaction. Bates and Taylor[2] reported that in the mercury sensitized reaction, which is generally conceded to go through the intermediate stage of atomic hydrogen, they were able to show hydrogen peroxide to be the sole product. This fact was in complete agreement with the mechanism originally suggested by Taylor and Marshall, which may be written

$$\begin{array}{lr} Hg' + H_2 \longrightarrow Hg + 2H & (1) \\ H + O_2 \longrightarrow HO_2 & (2) \\ HO_2 + H_2 \longrightarrow H_2O_2 + H & (3) \\ H + H \longrightarrow H_2 & (4) \end{array}$$

This mechanism has chain characteristics and, therefore, can have a quantum yield of hydrogen peroxide of any magnitude, depending upon the relative efficiency of the processes involving oxidation compared with the recombination of hydrogen atoms. Thus if (2) and (3) are relatively rapid and (4) is slow, we might have chains much greater than unity, while if the reverse were true, yields of unity or less might be expected.

Another possible mechanism was postulated by Bonhoeffer and Haber[3]

$$\begin{array}{lr} H + O_2 \longrightarrow HO_2 & (2) \\ HO_2 + H_2 \longrightarrow H_2O + OH & (3a) \\ OH + H_2 \longrightarrow H_2O + H & (4a) \\ OH + OH \longrightarrow H_2O_2 & (5a) \end{array}$$

We see that the initial process is the formation according to (3a) of water and an hydroxyl group. The latter may react according to (4a), giving water and hydrogen atom, again a chain process. If, however, the latter process required a large activation, it would occur so seldom as to allow practically all of the hydroxyls to form hydrogen peroxide according to (5a). If the latter condition exists, the quantum yield of hydrogen peroxide formation is unity, and, what is most important, there are formed

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(1) Taylor, THIS JOURNAL. 48, 2840 (1926), contains references up to this date; Marshall, *J. Phys. Chem.*, 30, 34, 1078 (1926); THIS JOURNAL, 49, 2763 (1927); Haber and von Schweinitz, *Sitzb preuss. Akad. Wiss.*, 30,499 (1928); Farkas, Haber and Goldfinger, *Naturwissenschaften*, 17,674 (1929); 18, 266 (1930); Haber, ibid., 18, 917 (1930): Farkas, Haber and Harteck, *ibid.*, 18, 266, 443 (1930); *Z. Elektrochem.*, 36, 711 (1930); Frankenburger and Rlinkhardt, *Z. physik. Chem.*, 8B, 138 (1930); 15B, 421 (1932); *Trans. Faraday Soc.*, 27,431 (1931).

(2) Bates and Taylor, THIS JOURNAL, 49,2438 (1927)

(3) Bonhoeffer and Haber, Z. *physik. Chem.*, 137A, 263 (1928); Z. *angew. Chem*, 42, 475 (1929); see also Farkas, Haber and Harteck, *Naturwissenschaften*, 18, 266 (1930).

simultaneously at least two molecules of water. There must appear, therefore, at least **51.4** weight per cent. of water in the products. This mechanism has received general recognition, in spite of the work of Bates and Taylor already cited, and of Bonhoeffer and Boehm,[4] who found **75%** of hydrogen peroxide in the products of the reaction of molecular oxygen with hydrogen atoms produced by a discharge.

Another possible point of divergence is the quantum yield of hydrogen peroxide. If this were of a magnitude greater than unity the Haber mechanism would be ruled out. **A** yield, however, of unity or less would be entirely inconclusive. Marshall's measurements of the quantum yield[4a] gave a value of 6.6. More recently Frankenburger and Klinkhardt have redetermined this magnitude and find a value near unity, which they advance as strong proof of the Haber mechanism. Since, however, they find that in fifteen out of twenty-three experiments recorded the value was somewhat greater than unity, these authors have introduced an alternative reaction to (3a)

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

This would lead to a quantum yield of three, and they then explain their high values by suggesting that both (3a) and (6a) take place, giving a value intermediate between 1 and **3.** This supposition rules out the later work of Marshall[5] as a basis for distinguishing between the two mechanisms, because he used moist gases in obtaining **100%** hydrogen peroxide formation.

It immediately appears that considerably more importance is to be attached to the early work, which showed hydrogen peroxide as the sole product in dry gases, than was supposed at that time. This work has, therefore, been repeated with great care with a view to settling this point and thereby differentiating between the two postulated mechanisms. The great frequency with which the Haber mechanism has been introduced into various reaction kinetics during the past years makes this simple yet crucial experiment seem of great importance![6]

The effect of water vapor on the production of hydrogen peroxide ha. also been studied in an effort to test the validity of reaction (6a).

Experimental

Tank hydrogen and tank oxygen were used without purification, since the possible impurities, nitrogen, etc., have been shown by Marshall to be without effect on the reaction.

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[4] Bonhoeffer and Boehm, Z. *physik. Chem.*, 119,385 (1926): Bonhoeffer and Loeb, *ibid.*, 119,474 (1926).

[4a] In a note published since this article was written, Marshall has revised this value to 2.6 [THIS JOURNAL, **54**, 4460 (1932)].

[5] Marshall, THIS JOURNAL, 49, 2763 (1927).

[6] Bodenstein, *Trans. Faraday* Soc., **27**, 413 (1931); von Elbe and Lewis, THIS JOURNAL, **54**, 552 (1932); Lewis, *Chem. Rev.*, **10**, 49 (1932); Norrish, *Trans. Faraday Soc.*, 27,461 (1931); *Proc. Roy. Soc.*, (London) **A135**, 332 (1932); Alyea, THIS JOURNAL, **53**, 1324 (1931); Kassel, "Kinetics of Gas Reactions," Am. Chem. Soc. Monograph No. 57, p. 121.

In all the experiments a flow system was used. The rate of flow was measured by flowmeters previously calibrated against a standard gasometer. The gases, before entering the reaction zone, were separately bubbled through wash bottles containing mercury, and, after the streams of hydrogen and oxygen were united, they were once more bubbled through mercury to ensure saturation and complete mixing. The gas mixture was then either dried over phosphorus pentoxide, or else passed through a medium which regulated the water vapor pressure to a desired amount. On leaving the illuminated zone, the gases were led into a trap or traps immersed in liquid air. Quartz to Pyrex seals and ungreased ground glass joints were used to prevent as much as possible any decomposition of the peroxide which might occur from contact with rubber or other foreign materials.

Two methods of illumination were employed. In the first, an ordinary vertical arc of the Cooper–Hewitt type was immersed in a water-bath maintained at 14°. Surrounding this, and also under water, was a quartz spiral of 4.5 cm. diameter, made of 140 cm. of 5-mm. bore quartz tubing. The arc burned at 6 amperes and 21 volts. The second method of illumination made use of the special type of mercury arc described in detail by Bates and Taylor.[2] The reaction tube is surrounded by the arc, and the gases flow through in a straight line. In our set-up, the reaction tube was of quartz, 8 mm. in bore and 40 cm. long.

Procedure

In making a run, the arc was first started and allowed to come to a constant condition. The gases were turned on, and their rates of flow adjusted to the desired values; they were not permitted to flow through the reaction zone until a moment before a run was started, in order to avoid as much as possible the formation and deposition of mercuric oxide at the outlet from the reaction zone, since it was found that an accumulation of this yellow oxide materially reduced the yield of hydrogen peroxide. When all was ready, the gases were passed through the reaction zone for one minute, and the trap, previously weighed and now immersed in liquid air, was attached by the ground glass joint to the outlet. In order that frost should not form at the outlet and later melt and run back into the trap, the off-gases were led out through a length of rubber tube attached to the trap. After the reaction had been permitted to proceed for the desired time (usually ten minutes), the trap was removed from the liquid air, warmed up to room temperature and weighed. The reaction products were then rinsed out with distilled water, and titrated for hydrogen peroxide with 0.1 *N* potassium permanganate. The operations of weighing and titration were carried out as expeditiously as possible in order to minimize the amount of peroxide decomposed during the time. From the total weight of the product, and the amount of hydrogen peroxide as determined in the titration, the percentage yield of the hydrogen peroxide could be calculated.

Experimental Results

Dry Gases.—It has been stated previously that the gases were dried in the experiments by passing them over phosphorus pentoxide. In order to indicate the efficiency of this process several blank runs were made at various times during the investigation, and in no instance was any weighable moisture frozen out in the traps.

The results with the quartz spiral and small mercury lamp are recorded in Table I, experiments 1 to 7. Various rates of flow and different ratios of hydrogen to oxygen were tried. It was observed that mercury oxide was deposited on the last coil of the spiral and that it considerably decreased the peroxide yield from any subsequent run. Consequently, the practice was adopted for the later experiments of cleaning out the spiral with dilute nitric acid before each test. The data show that in all except the first two experiments, the weight per cent. of hydrogen peroxide in the product was greater than the 50% yield to be expected according to Frankenburger. In one instance it was as high as 75%.

Using the special type of mercury arc, more experiments were carried out with dry gases. A rate of flow of about 135 liters per hour and an eight to one hydrogen to oxygen mixture gave the best results. Here as with the other set-up an accumulation of mercury oxide at the outlet of the reaction zone cut down the peroxide yield. The results are shown in Table I, experiments 12 to 21.

TABLE I

RUNS WITH DRY GASES

No.	Rate of flow liters/hr. O_2	Hz	Ratio Hz: 0 2	Time of run, min.	Total product, mg.	H_2O_2, mg.	H_2O_2 %
1	20	105	5:1	5	11.5	4.4	38.5
2	20	102	5:1	5	17 7	5 4	30.7
6	25	120	5:1	10	8.5	5.6	65.5
3	14	130	*9*:1	20	23.6	16.1	68.5
4	12	129	11:1	20	19.1	10.3	54.0
5	12	127	11:1	10	9 8	*7.3*	74.9
7	8	140	17:1	11	10.1	7.3	72.6
12	29	117	4:1	5	5 8	3.4	58.0
13	20	118	6:1	10	16.8	13.6	81.0
14	20	118	6:1	10	12 5	9.7	77.2
24	22	151	7:1	10	11.3	7.7	67.9
17	10	73	7:1	10	10 2	7.4	72.5
15	15	118	8:1	10	9.2	7 5	82.0
16	15	118	8:1	10	11 3	9.1	80.5
22	14	120	8.5:1	10	10.5	5 5	52.0
23	14	119	8.5:1	10	11.0	*7.5*	68.1
11	12	118	10:1	5	7 8	4.4	57.0
21	12	130	11:1	10	14.0	10.2	73.2

Experiments 1 **to** 7 **with quartz spiral; experiments** 12 **to** 21 with **special arc.**

They indicate that again more than **50%** by weight of peroxide could be obtained, and that in fact a yield of over **80%** was found in two cases.

It seemed possible that in the freezing-out process hydrogen peroxide might be trapped more easily than water, thereby leading to high peroxide yields. It was not expected that a preferential condensation of the peroxide could be occurring by reason of a difference in vapor pressure of the two substances for at liquid air temperatures the vapor pressures of both must be negligibly small. Nevertheless, a purely mechanical separation might be effected, for while the peroxide might be trapped out completely, the water might be caught only partially, since it is known that water tends to be carried through a liquid air trap in the form of a mist or "snowstorm."

Consequently, a second trap (Trap No. 2) of the ordinary type was attached in series with the first (Trap No. 1) by means of a ground glass joint, and more experiments were made. These showed that a considerable quantity of the product was carried through the first trap and caught in the second. But what is more to the point, the water was as readily trapped out as the peroxide, for the percentage of the latter was the same in both traps. Table II, experiments 2 to **23,** contains a **résumé** of these results. In this set of experiments, peroxide yields as high as 88% were obtained, while the average of seven tests was 82.5%.

Inasmuch as all the product might not be caught even in two traps, the second was replaced by another trap of *a* different type. This consisted of a series of five U-tubes made from a single long length of 6-mm. Pyrex tubing. The bends were made sharply so that all five could be put into one Dewar flask containing the liquid air. This multiple trap was attached to the first by a ground glass joint, so that in reality there were six traps in series. During a run, the top bends of the multiple trap were kept warm by a blast of hot air. Thus any "snowstorm" of water or peroxide must have been melted during its passage from one U to the next, thereby ensuring a more complete condensation of the product.

In accordance with expectations, experiments showed that a large portion of the total amount of the substance was frozen out in this multiple trap. Liquid was condensed in progressively smaller amounts on each down tube of the successive U's. On the fourth down tube, the amount condensed **was** just visible, while on the last, little or no product was observable. The conclusion was reached that with this device essentially complete recovery of the product was accomplished. As in the previous work with the double trap the percentage of hydrogen peroxide **was** the same in the multiple as

TABLE II

RUNS WITH DRY GASES AND SPECIAL ARC

Total rate of flow, 136 liters/hr. Ratio $H_2:O_2 = 8:1$

No.	Time of run, min.	Total product, mg. Trap No. 1	Total product, mg. Trap No. 2	Ratio $\frac{\text{Mg. in No. 1}}{\text{Mg. in No. 2}}$	H_2O_2, mg. Trap No. 1	H_2O_2, mg. Trap No. 2	Ratio $\frac{H_2O_2 \text{ in No. 1}}{H_2O_2 \text{ in No. 2}}$	H_2O_2, % Trap No. 1	H_2O_2, % Trap No. 2
1	10	14.1	6.0	2.35	10.6	4.1	2.46	75.0	68.0
2	10	12.6	5.6	2.25	11.0	4.5	2.56	86.5	79.0
8	10	12.1	5.4	2.24	9.0	4.1	2.40	80.6	72.5
11	10	12.2	5.3	2.30	10.8	4.7	2.32	87.8	87.5
14	10	11.3	5.2	2.17	9.6	4.6	2.12	85.5	87.4
21	10	11.9	5.5	2.16	10.0	4.7	2.11	83.5	85.6
23	10	12.4	6.1	2.03	11.0	5.3	2.06	88.5	87.0
29	10	14.5	12.0	1.21	10.1	6.5	1.56	70.0	54.5
31	10	13.5	10.0	1.35	11.3	8.1	1.40	83.3	80.5
32	10	13.8	10.0	1.38	11.8	8.3	1.40	82.2	82.6
33	10	15.0	9.4	1.60	13.4	7.9	1.70	89.0	83.5
41	10	12.1	7.9	1.53	10.3	6.8	1.51	84.8	86.0

Double trap, runs 2 to 23; multiple trap. runs 29 to 41.

in the first trap, indicating again that the peroxide was not preferentially condensed. The data are tabulated in Table II, experiments 29 to 41.

The results of all the preceding experiments with dry gases demonstrate conclusively that 85% by weight of hydrogen peroxide can be obtained easily in the condensable product from the mercury sensitized hydrogen–oxygen reaction.

Moist Gases.—In the first experiments to determine how moisture in the gases influences the hydrogen peroxide yields, only the total amount of peroxide appearing in the product was ascertained. Alternate runs were made, using first dry and then moist gases, in order to bracket and check the results. To regulate the moisture in the gases, they were by-passed either through a long tube containing granular calcium chloride, or through a trap containing cracked ice, the trap itself being maintained in an ice-bath. These two environments ensured a partial pressure of water in the gases of about 0.4 mm. and 4 mm., respectively. When using ice to maintain the water vapor pressure, the ice trap was put in the gas train before the mercury saturators in order that the mercury pressure in the gases might not be altered.

The observations obtained using the special type of mercury arc as a source of illumination are recorded in Table III, experiments 18a to 18f indicating the results with 0.4 mm. of water, experiments 19a to 20c with 4 mm. of water.

TABLE III

RUNS WITH MOIST GASES AND SPECIAL ARC

No	Condition of gases	Rate of flow liters/hr. O_2	H_2	Ratio H_2/O_2	Time of run. min.	H_2O_2, mg.
18a	Dry	15	118	8:1	10	8.3
18b	Wet	15	119	8:1	10	9.5
18c	Dry	15	120	8:1	10	5.6
18d	Wet	16	118	8:1	10	9.3
18e	Dry	15	120	8:1	10	9.6
18f	Wet	15	120	8:1	10	12.0
Gases dried over phosphorus pentoxide. Gases wet over calcium chloride.						
19a	Dry	15	120	8:1	10	9.9
19b	Wet	15	120	8:1	10	5.9
19c	Dry	15	120	8:1	10	7.5
19d	Wet	15	120	8:1	10	8.0
19e	Dry	12	120	8:1	10	7.0
20a	Dry	12	130	11:1	10	9.0
20b	Wet	12	130	11:1	10	8.7
20c	Dry	12	130	11:1	10	8.7
Gases dried over phosphorus pentoxide. Gases wet over ice.						

As examination of the results apparently indicates that when the lower pressure of water was used, the peroxide yield was very slightly increased over that obtained with *dry* gases. However, but little trust is to be placed in this conclusion, since the magnitude of the observed differences between the yields with wet and dry gases may be within the experimental error. Certainly with the higher concentration of water, no differences between the wet and dry runs are to be found, since the amounts of peroxide procured in the alternate runs agree well within the experimental deviation.

A number of runs, in which two traps were placed in series to catch the products, were conducted using moist gases. In these experiments, only calcium chloride was used as a means for regulating the moisture content of the gas mixture. The amount of water which could be recovered from the moist gases was ascertained by making several blank runs. Such a determination was accomplished by weighing the water caught in the two traps, and also by observing the increase in weight of a small phosphorus pentoxide tube attached directly to the outlet from the reaction zone. The phosphorus pentoxide tube caught about 1 mg. more moisture than the total amount found in the two traps. This was not surprising in view of the fact, already shown, that two traps cannot catch all the product. The amount of water recovered was about that to be expected if 0.3 to 0.4 mm. partial pressure of water existed in the gases. The results given in Table IV, experiments 12 to 22, are to be compared with those of Table II, experiments 1 to 23, for the runs with the moist gases were alternated with those of the dry gases recorded in that table. In Table IV, the amounts of moisture collected in the blank runs are also recorded, experiments 4 to 24.

These results indicate very definitely that with 0.4 mm. of water vapor in the gases, the total hydrogen peroxide yield is not altered to an observable extent. Moreover, since the ratio H_2O_2 in No. 1/H_2O_2 in No. 2, is the same whether the gases be originally wet or dry, it is apparent that the presence of water does not affect the relative amounts of hydrogen peroxide caught in the two traps. This conclusion is also warranted by the fact that the percentage yields of hydrogen peroxide recorded in Table IV are identical for both traps.

Finally, the work was repeated using the multiple trap. Here again, a study of the data of Table IV, experiments 36 to 43, together with those of Table II, experiments 29 to 41, shows that moisture in the gases does not increase the yield of hydrogen peroxide nor alter the relative amounts of product caught in the respective traps.

Using ice as the medium to supply the moisture some experiments were carried out with the quartz spiral set-up. Alternate runs with wet and dry gases were made, only the total amount of hydrogen peroxide formed being determined. It appeared that with this particular experimental arrangement, the total amount of peroxide was actually reduced more than 40% by the presence of 4 mm. of water in the gases. We have no explanation for this result, but present it as further evidence that hydrogen peroxide is decomposed during the course of the reaction.

TABLE IV

RUNS WITH MOIST GASES AND SPECIAL ARC

Total rate of flow, 136 liters/hr. Ratio $H_2 : O_2 = 8 : 1$. Time of run, 10 min.

No	Total condensate, mg Trap No. 1	Trap No 2	Ratio Mg. in No. 1 / Mg. in No. 2	H_2O_2, mg. Trap No. 1	Trap No. 2	Ratio H_2O_2 in No. 1 / H_2O_2 in No. 2	H_2O_2, % Trap No 1	Trap No. 2	Average H_2O in incident gases, mg. Trap No. 1	Trap No. 2	Products of reaction Total, mg. Trap No. 1	Trap No. 2	H_2O_2, % No 1	No. 2
12	17.9	7.2	2.49	10.8	4.5	2.40	59.8	62.0	6.3	1.6	11.6	5.6	93	80
13	18.0	7.8	2.31	10.3	4.7	2.19	57.3	60.0	6.3	1.6	11.7	6.1	88	78
20	18.5	7.2	2.57	10.5	4.3	2.44	56.4	59.5	6.3	1.6	12.2	5.6	86	78
22	19.1	8.5	2.24	11.5	5.0	2.30	59.5	58.4	6.3	1.6	12.8	6.9	90	73
Blank runs (arc off)														
4	6.0	1.3	4.6											
5	6.0	1.1	5.3											
10	5.2	1.6	3.7											
15	6.8	1.8	3.8											
16	6.8	1.6	4.2											
18	6.6	1.7	3.9											
24	6.3	1.9	3.3											
36	16.0	12.5	1.3	9.1	6.5	1.4	56.8	52.1	4.6	3.3	11.4	9.2	80	71
37	18.7	13.4	1.4	10.5	7.0	1.5	56.0	52.0	4.6	3.3	14.1	10.1	75	70
42	19.0	14.3	1.3	..	7.4	..	..	53.0	4.6	3.3	14.4	11.0	..	72
43	18.3	13 6	1.3	9.8	7.6	1.3	51.5	54.0	4.6	3.3	13.7	10.3	67	69
Blank runs (arc off)														
34	4.0	3.2	1.3											
35	5.1	3.4	1.5											

Double trap, experiments 4 to 24; multiple trap. experiments 34 to 43.

Discussion of Results

It is quite obvious that the original Haber mechanism is not capable of accounting for percentage yields of hydrogen peroxide of the order of 85%. Thus we can rule this out as giving a complete description of the processes occurring in the reaction. It should be emphasized that the values of the percentage composition of peroxide in the products are minimum values. All experimental errors would tend to decrease it. For example, in weigh; ing the trap in which the products are condensed after drying at room temperature or above, then immersing it in liquid air and again weighing after allowing it to warm up and drying with a towel, it would perhaps be expected that the weight in the latter case might be higher than the former due to condensation of moisture from the atmosphere. This would result in an apparent increased total weight of products and consequently a smaller observed percentage of peroxide.

Any objection to these results based upon the supposition that the peroxide is caught preferentially and water allowed to go through the trap is ruled out by the facts that the same percentage of peroxide is found in subsequent traps as in the first and also that in moist gases the water is caught as well or better than peroxide.

It is to be observed that, since we have been able to show the products of the reaction to consist of from 85–100% hydrogen peroxide, as compared with the smaller percentage reported by Frankenburger and Klinkhardt, their quantum yield must have been higher than their calculations show. Most or all of the water reported by these authors in their products must result from subsequent decomposition of peroxide. This would mean that their quantum yield of peroxide is in reality at least **3** molecules per quantum. These authors did not report the water formed in their individual experiments. If, therefore, the two to one ratio of water to hydrogen peroxide, which they claim to be present in some runs, persisted in all their runs, then in reality they were obtaining average values of **3.6** and maximum values up to **6** molecules per quantum. Such values would be in good agreement with those reported by Marshall. Furthermore, mercury is known to bring about decomposition of hydrogen peroxide? Indeed, we have actual proof that this occurs to some extent. When the products in the trap are first observed mercury appears as a black deposit. After warming and weighing this can be seen to have changed to the characteristic yellow of mercuric oxide. Due to these facts, together with the possibility of decomposition in the reaction zone, of which there is evidence in the appearance of mercuric oxide, the authors are inclined to the view that hydrogen peroxide is the sole primary product of the reaction.

However, the suggestion of Frankenburger and Klinkhardt that the reaction

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(7) Elder and Rideal, *Trans. Faraday Soc.*, **23**, 550 (1927).

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

might play a part in the reaction must be considered in some detail in order to see if this process will account for the high peroxide yields, even in dry gases. This suggestion may be formulated

$$K_1 \quad HO_2 + H_2 \longrightarrow H_2O + OH \qquad (3a)$$
$$K_2 \quad HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

Reaction (3a) gives rise to one molecule of water and one-half molecule of peroxide; reaction (6a) to three-halves molecules of peroxide. We may then write

$$d\,\frac{[H_2O_2]}{dt} = \frac{[HO_2]\,[H_2]}{2}K_1 + \frac{3[HO_2]\,[H_2O]}{2}K_2$$

$$d\,\frac{[H_2O]}{dt} = [HO_2]\,[H_2]\,K_1 - [HO_2]\,[H_2O]\,K_2$$

dividing, we obtain

$$\frac{d[H_2O_2]}{d[H_2O]} = 1/2\,\frac{([H_2]\,K_1 + 3[H_2O]\,K_2)}{[H_2]\,K_1 - [H_2O]K_2}$$

$$2[H_2O_2] = \int_{[H_2O_0]}^{[H_2O_E]} \frac{[H_2]\,K_1 + 3[H_2O]\,K_2}{[H_2]\,K_1 - [H_2O]\,K_2}\,d[H_2O]$$

where $[H_2O_0]$ is the initial water concentration, and $[H_2O_E]$ the final. Integrating, and taking the limits, we obtain

$$2[H_2O_2] + 3([H_2O_E] - [H_2O_0]) = 4K\ln\frac{K - [H_2O_0]}{K - [H_2O_E]} \qquad (A)$$

where $K = K_1[H_2]/K_2$, and $[H_2]$ is considered constant.

If now we take the average values for $[H_2O_2]$, $[H_2O]$, and $[H_2]$ as found from the data in Table II, runs 2–23, and express them in mm., we find $[H_2O_0] = 0$, $[H_2O_E] = 0.122$ mm., $[H_2O_2] = 0.359$ mm., $[H_2] = 675$ mm. These substituted in equation (A) give $K = 0.144$, or $K_2/K_1 = 4700$, which means that HO_2 would react at least 4700 times as fast with H_2O as with H_2, or that the activation energy of reaction (3a) would be some 5.0 Cal. greater than reaction (6a), which is not at all an impossible result, in spite of the fact that process (3a) is some 80 cal. more exothermic than (6a).

However, if we now take the data from Table IV (runs 12–22) in which moist gases were studied and find the pressures of the reactants and resultants, we find $[H_2O_0] = 0.360$ mm., $[H_2O_E] = 0.482$ mm., and $[H_2O_2] = 0.371$ mm. as the average values. These give a $K = 0.76$, over five times the value determined in the dry gases, a difference which is much larger than the experimental error, and indicates that water has no effect on the reaction. The above data used in the calculations of K_2/K_1 are those of our results which present the most favorable case for the Frankenburger mechanism. However, only about 75% of the total product was caught using the double trap, so the value of the partial pressure of H_2O_2 and H_2O used in the above calculations should be increased some 25%. This does not change to any great extent the value of K_2/K_1 calculated for the dry gases, but makes the discrepancy between the constants in the dry and moist gases even more marked. This is shown by taking the data from Table II, runs 31-41, and Table III, runs 36 to 43, where, for the dry gases $[H_2O_2] = 0.465$ mm., $[H_2O_0] = 0$, $[H_2O_E] = 0.164$, whence $K = 0.195$; for the moist gases, $[H_2O_2] = 0.405$ mm., $[H_2O_0] = 0.360$ mm., $[H_2O_E] = 0.665$, where $K = 1.75$. Thus K for the wet gases is some 9 times greater than K for the dry, which is somewhat greater than that obtained above. This can also be indicated from the fact that the amounts of hydrogen peroxide and water produced in the moist gases are practically the same as those in dry gases, in spite of the increase in water concentration, thus 0.371 mm. as against 0.359 mm., and 0.482—0.360 = 0.122 mm. According to the value of K obtained from the dry gases, we should expect, if this were the true mechanism, that the water concentrations should have actually decreased in the moist gases experiments. This can be seen from the fact that at equilibrium

$$[H_2]\,K_1 = [H_2O]\,K_2$$
$$[H_2O] = [K_1]\,[H_2]/K_2 = K = 0.144$$

Therefore, starting with $[H_2O_0] = 0.360$, we should expect $[H_2O_E]$ to lie between 0.360 and 0.143, instead of being greater than 0.360. Thus we can find no support for the Haber mechanism as modified by Frankenburger and Klinkhardt.

The mechanism of Marshall and Taylor has been criticized by Frankenburger and Klinkhardt for two reasons. First, they object because it postulates the necessity of an association reaction

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

But this actually has no basis, since the other mechanisms have the same assumption. The three-body reaction is in reality two consecutive bimolecular reactions, with the additional requirement that collision of the quasi-molecular association with its next reaction partner must come within its life-time, whatever that may be. The second criticism is that, if we assume that the two hydrogen atoms which add to oxygen each result in 69 cal. of energy, the reaction

$$HO_2 + H_2 \longrightarrow H_2O_2 + H - 31 \qquad (3)$$

would be 31 calories endothermic. On the same basis the reaction

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH - 42 \qquad (6a)$$

would be 42 calories endothermic.

A further objection that reaction (3) would never take place, because the hydrogen atom would react with the hydrogen peroxide to give the more exothermic result

$$HO_2 + H_2 \longrightarrow H_2O + OH + 33 \qquad (3a)$$

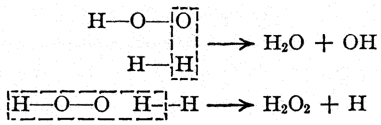
or

$$H + O_2 + H_2 \longrightarrow H_2O + OH + 112$$

instead of

$$H + O_2 + H_2 \longrightarrow H_2O_2 + H + 38$$

is not justified. Reaction (3a) most probably requires a higher activation energy than reaction (3), because in general the activation energies of processes involving a mutual interchange of partners and the breaking of two bonds are greater than those of simple replacement



$$\mathrm{H{-}O{-}O} + \mathrm{H{-}H} \longrightarrow H_2O + OH$$

$$\mathrm{H{-}O{-}O\ \ H{-}H} \longrightarrow H_2O_2 + H$$

The calculation of the activation energy of the reaction $OH + H_2 \longrightarrow H_2O + H$ from Frankenburger and Klinkhardt's data, used by them to support the validity of their assumptions, is of no value for two reasons. First, we have shown that it is possible to obtain very high peroxide percentages which would invalidate their results and second the value of this energy obtained from the data of Farkas, Haber and Harteck, and with which they found agreement, is now recognized as not being characteristic of this process at all.[8] The present authors see no necessary connection between reactions in the gas phase and the cathodic formation of hydrogen peroxide at a rate of one mole per mole of hydrogen ions liberated, which Frankenburger and Klinkhardt advance as support for their mechanism. However, even granting a correspondence between the cathodic and gas phase reactions, we can see no discrepancies between this equivalence and the mechanism postulated on page 110.

The original mechanism of Taylor and Marshall meets with none of these difficulties and the authors are inclined to believe it to be the true one. Since this reaction scheme has chain characteristics, why are the quantum yields of both Marshall, and Frankenburger and Klinkhardt so low? This difficulty can be met by a slightly modified mechanism. The heat of formation of hydrogen peroxide from $H + H + O_2$ is 138 kilocalories. Assuming that this energy is divided equally between the two steps *(2)* and (3), the complex HO_2 is endowed with 69 calories at the instant of its formation. It is, therefore, an activated molecule, and may have an appreciable life. If its first collision after formation is with a hydrogen molecule, the reaction to give H_2O_2 and H can easily take place, since the internal energy of the complex can overcome the endothermicity of the reaction step.

A series of possible processes could be

$$H + O_2 \longrightarrow HO_2' \qquad (2b)$$

$$HO_2' + Hz \longrightarrow H_2O_2 + H \qquad (3b)$$

$$HO_2' + O_2 \longrightarrow HO_2 + O_2' \qquad (6)$$

$$\text{or } HO_2' + O_2 \longrightarrow H + 202 \qquad (7)$$

$$\text{or } HO_2' \longrightarrow H + O_2 \qquad (8)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (9)$$

$$H + H \longrightarrow H_2 \qquad (4)$$

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(8) Haber and Oppenheimer, Z. *physik.* Chem., **16B**, 443 (1932); unpublished work in this Laboratory; see Taylor and Salley, THIS JOURNAL, **55**, 96 (1933).

Such a mechanism involving activated complexes can explain the shortness of the chains at room temperature. Steps (6) and (8) indicate how the complex might be deactivated or disrupted; either process tends to give (9) and (4) more chance to take place. Step (9) might very possibly occur predominantly as a wall reaction, since this reaction is neither exothermic nor endothermic, but may require an activation energy. Any part of the reaction which goes through step (9) gives rise to one molecule of peroxide per quantum. If hydrogen atoms recombine according to (4) there is no yield of peroxide. Both of these reactions would, therefore, tend to lower the observed quantum yield.

These considerations have been based on the assumption of Frankenburger and Klinkhardt, that both hydrogen atoms adding to oxygen give the same energy. If, however, as is possible, the second hydrogen gives rise to a greater energy liberation, the endothermicity of reaction (3) is decreased. If the first hydrogen-oxygen bond were 38 cal. and the second 100 cal., reaction (3) would have no heat of reaction. This reaction would then occur on every collision if there were no activation energy involved. Considerations of this type, however, will lead us nowhere with our present lack of knowledge of the relative magnitude of these hydrogen–oxygen linkages.

It must not be forgotten that in the mercury sensitized reaction, mercury hydride, HgH, may be playing a role. A possible mechanism would be as follows

$$Hg' + H_2 \longrightarrow HgH + H \qquad (1a)$$
$$HgH + O_2 \longrightarrow HgO + OH \qquad (11)$$
$$H + O_2 \longrightarrow HO_2 \qquad (2)$$
$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (3a)$$
$$OH + OH \longrightarrow H_2O_2 \qquad (5a)$$
$$H + H \longrightarrow H_2 \qquad (4)$$

For every quantum of light absorbed, one hydrogen peroxide molecule and one water molecule would be formed, leading to a yield of 65% by weight of peroxide. However, even this is lower than the observed 85% yield, and so cannot account completely for the observed results. If some hydrogen atoms recombined, the peroxide percentage might be increased. This, however, would give rise to a quantum yield even less than unity. Further, mercury atoms are known to absorb many quanta of light in passing through the reaction zone, which would be improbable if mercuric oxide were formed in the process. For several reasons, then, we can eliminate such a mechanism.

The authors wish to thank Professor Hugh S. Taylor for his interest and valuable assistance in this work.

Summary

1. The yield of hydrogen peroxide from the mercury sensitized hydrogen–oxygen reaction is greater than 85%. The water formed is ascribed in

the main to secondary peroxide decomposition. It is concluded that hydrogen peroxide is the sole product of the reaction significant as regards reaction mechanism.

2. The yield of hydrogen peroxide is unaltered by the presence of water vapor in the gases. As a consequence, the reaction step $H + O_2 + H_2O = H_2O_2 + OR$ cannot be of any importance.

3. The Haber mechanism for the reaction of hydrogen atoms with oxygen molecules does not represent the only course of the reaction at ordinary temperatures. Peroxide formation must occur not only by combination of OH radicals but also by some other reaction.

4. Possible reaction mechanisms consistent with the results have been discussed.

PRINCETON, NEW JERSEY

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Effect of Particle Size upon Intensity in x-Ray Spectroscopic Analysis

BY GORDON R. FONDA

In a limited number of elements,[1] a lower intensity of the La doublet has been observed when the element was in the form of a metallic powder rather than in that of a polished metallic plate or even in that of an oxide. It persisted whether the crystal in the spectroscope was sodium chloride or aluminum oxide. No such difference was observed for the $K\alpha$ doublet. As such irregularities are liable to introduce serious errors in applications of x-ray spectroscopy to quantitative analysis, the subject has been studied further. The conclusion is that they are a consequence of too large particle size which brings about an abnormal absorption of the x-radiation emitted, particularly when it is in the longer wave length range. It is for this reason that it was first noticed in L radiation. The effect has been found to be present likewise in K radiation, though to a much less extent. It occurs under the experimental condition which generally holds—namely, that the emitted x-ray beam be examined at a different angle from that made by the exciting beam of electrons.

x-Radiation is excited throughout a certain depth of material, depending on the penetration of the electrons, and consequently encounters in its emission a corresponding amount of absorption by the material itself. If there are any irregular protrusions in the surface which lie in the path of the beam which is under observation, then the radiation is subjected to additional absorption as it passes through them. Such an effect should

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[1] Fonda, THIS JOURNAL, 54, 115 (1932).

be presented, for instance, by the surface of a powdered material whose particles are of sufficient size. It can be well demonstrated by examination of the intensity from a grid formed by winding wires closely together with their turns touching. Such a grid was used as a target above the window of the cathode ray tube, placed vertically and operated as before from a regulated dc. circuit at 0.2 ma. and 86 kv. It was held at an angle of 20° to the axis of the tube and the intensity of the α doublet in the radiation given off in a horizontal direction was measured with a Seemann spectroscope placed horizontally. The surface of the crystal in the spectroscope lay in a vertical plane. Measurements were first made with the grid so placed that the turns of wire lay in the axis of the spectroscope, a condition comparable to that of a smooth plate in that the surface irregularities formed by the grid wires were not interposed in the path of the x-ray beam. The intensity was, in fact, found to be the same as for a smooth plate within the limit of error.

The grid was then placed with the turns of wire normal to the axis of the spectroscope. Here the conditions are altogether different as compared with the plate. The x-radiation excited on the side of a grid wire turned away from the spectroscope must pass first through the wire itself and a portion of that formed on the side toward the spectroscope must pass through the adjoining wire. This represents a greater thickness of material than the radiation from a smooth plate is subjected to and the absorption will be correspondingly greater. The loss in intensity will become less only as the size of the wire is decreased, thus lessening the additional absorption, or as x-radiation is chosen of shorter wave length for which the absorption coefficient is consequently lower.

Experiments were made with grids of molybdenum, copper and tungsten. The results are given in Table I. As the interest lies in the intensity from the grid when placed normal to the axis of observation, the value of this term is expressed as the ratio which its intensity bears to that measured when the grid was parallel to the direction of observation. There are geometrical reasons for the increase in the intensity ratio observed for the grid with the larger tungsten wire.

TABLE I

EFFECT OF GRID POSITION ON INTENSITY OF X-RADIATION

	Mo-Ka	Cu-Ka	W-*La*
Wave length x-radiation, Å.	0.708	1.537	1.473
Absorption coeff.	200	540	2700
Intensity ratio—51 μ wire diam.	0.93	0.67	0.41
Intensity ratio—127 μ wire diam.	0.78	..	0.53

These results are in accord with the conclusion that surface irregularities of whatever origin will lead to a loss in intensity by their interposition in the path of the beam. Such a loss was observed, for instance, in the L radiation of tungsten from a plate which had been roughened by sand blasting or even by etching. It is to be expected likewise from powdered material, in which its effect should increase with particle size and should be more pronounced for L radiation than for K because of the longer wave length of the former and the resulting higher values for the absorption coefficient.

These expectations are supported by examinations of several materials in the powdered form. In all the sample was held at a 20° angle to the axis of the tube. This is important because otherwise the relative value of the absorption factors is changed and a still different order of the intensities will be found in the case of those substances which are affected by these factors. The particle size was determined for each sample in terms of the diameter by examination with the microscope. One hundred or more particles of each lot were measured and a distribution curve plotted. The average diameter was found always to coincide with the peak representing optimum distribution and is therefore the value employed in the tables for the sake of brevity. All of the oxides experimented with had been prepared by chemical precipitation and are consequently so fine in size that no abnormal absorption effects could arise with them. They were frequently used as standards for calibration.

The first group of substances examined included metal powders whose intensities were compared with those from the corresponding oxides in mixtures with a comparison element. The results in terms of normal intensity as unity are given in Table II.

In the case of tungsten some direct intensity measurements also were made. In them the intensity from powder whose particles were of $1\ \mu$ size was found to be the same as that from a polished plate. Larger size particles gave reduced intensities. All the sizes investigated gave reproducible intensities denoting that even for the largest size a sufficient number of particles was involved to maintain the same average orientation under different distribution. For still larger sizes it is to be presumed that the intensity would become irregular depending upon the chance

TABLE II

INTENSITY FROM METAL POWDER AS DEPENDENT ON DIAMETER AND ABSORPTION COEFFICIENT

			Intensity for particle sizes of					
Metal	Radiation, Å.	Abs. coeff.	$28\ \mu$	$12\ \mu$	$8\ \mu$	$4\ \mu$	$2\ \mu$	$1\ \mu$
Sn	Kα-0.489	93					1.00	
Mo	Kα-0.708	200				1.00		
Cu	Kff-1.537	540			1.00			
Co	Ka-1.785	560				1.00		
Fe	Kα-1.932	590					1.00	
Pb	La-1.172	1380		0.70				
W	La-1.473	2710	0.41			0.60		1.00
Sn	La-3.592	ca. 14000					0.60	

orientation of those particles which were within the area subjected to cathode ray bombardment.

The second group comprised some crystalline sulfides whose brittleness allowed them to be ground up and graded by screening into different sizes. Intensity measurements were made directly under comparable conditions and Table III gives a comparison in terms of the intensity from the smooth face of a large, single crystal as unity.

TABLE III

EFFECT OF PARTICLE SIZE ON INTENSITY OF SULFIDES

Substance	Radiation, Å.	Abs. coeff.	Intensity at particle sizes of 520 μ	310 μ	220 μ	160 μ	51 μ	4 μ	2 μ
FeS	Ka-1.932	550	0.32	0.52	0.64	0.76	0.76	1.00	1.00
PbS	La-1.172	1380	.50	.32	.48	.48	.50	0.74	0.80

This serves to demonstrate that the effect may become equally pronounced in the case of K radiation if the particles are of sufficient size. As the average particle size of powders that have been ground for analysis is generally below 4 μ, it is apparent that irregularities are not apt to be encountered in K radiation but only in L. This was demonstrated further by the examination of some carbides. Columbium carbide at an average diameter of 5 μ gave an intensity of the Kα doublet at 0.744 Å. that was normal for its columbium content. Tungsten carbide, however, at an average size of 2 μ gave an intensity of its La doublet at 1.473 Å. that was only 81% normal.

Finally a more complex case was examined of a tantalite containing a small percentage of columbium. A definite analysis was obtained by fusing the ore first and finally obtaining by a precipitation method a pure mixture of tantalum and columbium oxides which was complete and which proved from gravimetric measurements to comprise 66.4% of the ore. Spectroscopic analysis of the oxide, which was so finely divided as to be capable of avoiding error due to particle size, gave values of 93.8% Ta_2O_5 and 7.1% Cb_2O_5 corresponding to a content in the original ore of 62.3% Ta_2O_5 and 4.7% Cb_2O_5. From these values it was possible to calculate what the normal intensity of tantalum and columbium radiation should be from the ore Table IV gives values for the observed intensity as determined from spectroscopic analysis of the ore at different particle sizes in terms of the normal intensity. In the case of tantalum, correction is made for the small absorption due to the presence of iron and manganese.

TABLE IV

EFFECT OF PARTICLE SIZE ON INTENSITY MEASUREMENTS FROM A TANTALITE ORE

Particle size	Percentage of normal intensity Ta-La, %	Cb-Kα, %
9.5 μ	44.1	62.0
4.2	86.6	...
2 5	98.6	100.0

Conclusion

The intensity of a diffracted x-ray beam has been found to be decreased by surface irregularities of the target in proportion to their magnitude and to the coefficient of absorption of the target material for the wave length involved. This effect was studied for grids of various size and powdered particles of metals and compounds of various diameter. For accuracy in quantitative chemical analysis based on x-ray spectroscopy attention must therefore be given to the fineness of the powdered samples, more especially when La radiation is involved.

SCHENECTADY, NEW YORK RECEIVED JULY 20, 1932
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Sodium-Lead Alloys. The Structure of the Compound Known as Na_4Pb

BY CHARLES W. STILLWELL AND WALTER K. ROBINSON

A number of recent investigations have shown that when copper, silver or gold is alloyed with cadmium, zinc, tin or aluminum, the same types of crystal structures often occur in each binary alloy even though the empirical formulas of the compounds differ. The type structure of any specific compound seems to depend upon the ratio between the number of atoms and the number of valence electrons in the molecule.[1]

The behavior of binary alloys of these three metals is fairly consistent and it is of considerable interest to know whether similar relations hold for alloys in which the first group metal is an alkali metal. The only x-ray study of such alloys which has been reported is that for the lead rich end of the sodium–lead system, up to 32 atomic per cent. of sodium.[2] An extension of the data for this system is therefore desirable. The present paper presents an analysis of the crystal structure of the compound usually designated as Na_4Pb.

Experimental Part

The alloy was prepared by melting together in an iron crucible the theoretical quantities of sodium and lead, making due allowance for the evaporation of some sodium. Cooling curves showed the initial break at the melting point of the compound Na_4Pb indicated in the equilibrium diagram.[3] The alloy was annealed for sixty hours at 280–300° in an atmosphere of argon.

A Mueller tube and CuK_α radiation were used for obtaining the diffraction patterns. The camera was essentially the Debye–Scherrer type tipped on edge so that it rested on the curved surface instead of on the base of the cylinder. With this arrangement the specimen may be mounted at the center of curvature and kept covered with mineral oil

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(1) Westgren and Phragmen. *Trans. Faraday Soc*, **25**, 379 (1929).
(2) Zintl and Harder, Z. *physik.* Chem., *154*, 79 (1931).
(3) Calingaert and Boesch, THIS JOURNAL. **45**, 1901 (1923).

to prevent oxidation during the exposure. The x-ray beam is thus diffracted from the surface of a single piece of the alloy and good patterns may be obtained in a relatively short time. There are several obvious sources of error in this type of camera, but repeated calibration with pure metals has demonstrated that the maximum error in the determination of the interplanar spacings is 0.5%, and in general the error is somewhat less.

Complete diffraction data for the compound are listed in Table I. The values in column II are average values from four different films made from four different specimens of the alloy.

TABLE I

DIFFRACTION DATA FOR THE COMPOUND Na_4Pb ($Na_{31}Pb_8$)

Int.	Cm.	$\sin^2 \theta$	d_{hkl}	$h^2 + k^2 + l^2$	a_0
vs	3.96	0.0802	2.719	24	13.30
m	4.23	.0914	2.547	27	13.25
m	4.61	.1071	2.353	32	13.30
m	4.91	.1215	2.209	36	13.25
w	5.70	.1609	1.920	48	13.30
s	5.95	.1746	1.843	52	13.29
s	6.23	.1887	1.772	56	13.27
w	6.38	.1991	1.726	59	13.25
s	7.08	.2410	1.569	72	13.30
m	7.28	.2538	1.528	76	13.30
vw	7.76	.2839	1.445	84	13.23
s	8.35	.3233	1.354	96	13.28
w	8.53	.3356	1.329	99	13.21
w	8.74	.3505	1.301	104	13.28
w	8.97	.3655	1.274	108	13.26
m	9.46	.4003	1.217	120	13.31
m	9.65	.4140	1.197	123	13.29
w	9.86	.4287	1.176	128	13.30
w	10.23	.4564	1.140	136	13.29
w	10.54	.4791	1.112	144	13.33
w	11.06	.5157	1.072	152	13.21
m	11.93	.5782	1.013	171	13.25
w	12.31	.6057	0.9894	180	13.27
w	13.06	.6570	.9500	195	13.25
w	14.23	.7347	.8983	216	13.21
w	14.56	.7560	.8855	224	13.27
				Av.	13.27 ± 0.035 Å.

Discussion

The analysis indicates a face-centered cubic lattice in which $a_0 = 13.27 \pm 0.035$ Å. The error indicated is 0.5%, the maximum error established by the calibration of the camera. It is evident that most of the values for a_0 are well within this limit.

The structure of this phase suggests that it is analogous to the y-phase of the copper, silver and gold alloys. Of these, Cu_5Zn_8, Cu_9Al_4 and $Cu_{31}Sn_8$ are typical examples. These are similar in that they have cubic structures with large unit cells and in each the ratio of valence electrons to atoms is as 21:13. They differ in detail. Thus Cu_5Zn_8 is body-centered cubic and contains 52 atoms in the unit cell;[4] Cu_9Al_4 is simple cubic and contains 52–49 atoms per unit cell;[5] $Cu_{31}Sn_8$ is face-centered cubic, containing 416 atoms per unit cell.[6] In order that the number of molecules in a unit cell may be a whole number, Bernal[7] assigns the formula $Cu_{41}Sn_{11}$ to this copper–tin phase.

If it is assumed, as it was for the y-phase of the copper–tin system, that the more exact formula for the compound Na_4Pb is $Na_{31}Pb_8$, then the 21:13 value for the ratio of valence electrons to atoms is satisfied. The density of $Na_{31}Pb_8$ has been determined as 3.31 at 25° and from this value the number of atoms in the unit cell has been calculated as 77.2. This is sufficiently close to 78 to indicate that there are two molecules in the unit cell.

Another check is furnished by the data of Zintl.[2] He has reported a face-centered cubic structure (Na_2Pb_5 and Na_4Pb_9), containing four atoms in the unit cell in which $a_0 = 4.872 - 4.883$ Å. The side of the unit cell of $Na_{31}Pb_8$ is about 2.72 times as long as the above and the volume of $Na_{31}Pb_8$ is therefore twenty times that of the smaller cell. From these figures the number of atoms in the unit cell of $Na_{31}Pb_8$ has been calculated as 80, which agrees significantly with the value 77.2 determined from the density.

We are grateful to Dr. G. Calingaert of the Ethyl Gasoline Corporation, who prepared the alloys for this study, and to Dr. G. L. Clark of this Department, who suggested a study of sodium–lead alloys.

Summary

Diffraction data for the compound usually designated as Na_4Pb have been analyzed. The analysis indicates that the structure of this compound is face-centered cubic, with $a_0 = 13.27 \pm 0.035$ Å. There are 78 atoms in the unit cell. It is apparently analogous to the familiar y-phase of copper, silver and gold alloys and its more exact formula is therefore $Na_{31}Pb_8$.

URBANA, ILLINOIS

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(4) Bradley and Thewlis, *Proc. Roy. Soc.*, (London) A112, 678 (1926).

(5) Bradley, *Phil. Mag.*, 6, 878 (1928).

(6) Westgren and Phragmen, *Z. anwg. allgem. Chem.*, 175, 80 (1928).

(7) Bernal, *Nature*, 122, 54 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY. UNIVERSITY OF ILLINOIS]

Atomic Chlorine and its Reaction with Hydrogen[1]

BY W. H. RODEBUSH AND W. C. KLINGELHOEFER, JR.

One of the most promising methods of studying the mechanism of gaseous reactions is the introduction of the various atomic species into the reaction mixture. The classical example of such a study is the work of Bonhoeffer on atomic hydrogen.[2] The most satisfactory method for the production of gaseous atoms is by the high frequency electrodeless discharge. If it is desired to pass the atoms into a reaction chamber, a too high frequency is disadvantageous because the discharge will travel along the tube and affect the reaction. The catalytic effects of walls, water, metals, etc., have been clearly demonstrated in the case of hydrogen atoms but it has been proved in this Laboratory that each species of atom is a law unto itself so far as these effects are concerned.

The Production of Chlorine Atoms.—The thermal and photochemical dissociations of the chlorine molecule have been demonstrated by a number of observers but no one has produced any considerable amount of atoms by this method. The first attempt to produce chlorine atoms in this Laboratory was made with a discharge between cooled copper electrodes in a long tube of the Wood type. The electrodes were not attacked and the discharge could be maintained over a considerable range of pressure but the gas was not dissociated. This type of apparatus was discarded in favor of the electrodeless discharge.

Experimental

Dissociation of Chlorine.—The apparatus is shown in Fig. 1. It consisted of a supply of chlorine, A, a bulb for the electrodeless discharge, E, a diffusion gage, H, liquid air trap, mercury vapor pump and oil pump. The chlorine, prepared from concentrated hydrochloric acid and potassium permanganate, was washed with water, dried by sulfuric acid and liquefied in a bulb of about 30 cc. capacity by a mixture of dry ice and acetone. Moisture was kept out of the vent tube by means of a U-tube kept in the cold bath. The chlorine bulb was connected to the apparatus through a capillary which controlled the flow. The bulb was held at a temperature of −80°.

The discharge was produced in a 200-cc. Pyrex bulb. The energizing circuit was connected as shown. A 2.5 k. v. a., 25,000 volt Thordarson transformer was used. The condenser D consisted of 14 plates, about 20 by 23 cm., separated by about 5 mm. of window glass, the whole being immersed in insulating oil. The spark gap, F, of about 1 cm. width, had zinc electrodes about 3 cm. in diameter. The gap was mounted in a sound-proof box fitted with an air connection for cooling the electrodes and regulating the voltage drop. The coil, which was fitted closely to the bulb, was made in two parts of five turns each. It was carefully grounded near the center in order to reduce the stray discharge into the remainder of the apparatus. When this was properly done no discharge could be seen in a dark room at more than about 5 cm. distance from the bulb.

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(1) A *preliminary notice of this work has been published in the Proceedings of the National Academy of Sciences,* **18,** **531** **(1932).**

(2) *Bonhoeffer, Z. physik. Chem., 113,* **199** **(1924).**

All of the connections in the high frequency circuit were made with 3-mm. copper tubing. The current in the primary of the transformer was usually about 15 amperes and was regulated by a series resistance, B, and the air flow at the spark gap to give the best glow discharge.

The diffusion gage H was used to detect the atoms produced. It was similar to the gage described by Wrede.[3] It consisted of an orifice 0.1 mm. in diameter and gages for measuring the total and differential pressures. The orifice was made in a thin glass film sealed on the end of a 5-mm. tube which extended into the gas stream at a point about 7 cm. from the discharge bulb. The film was made by blowing out a glass bubble until it was thin enough to show colors. It was sealed to the tube by heating the latter and sticking it into the glass bubble. The hole in the film was made by placing it between two needle points between which a spark was passed by means of an induction coil. The size of the hole was controlled by the energy of the spark. The gages were of 5-mm. tubing and were filled with a heavy paraffin oil which was found to be unaffected by the chlorine. Gage J measured the total pressure; I, the pressure difference across the orifice. A cathetometer sensitive to 0.01 mm. was used to read the oil levels. The gage was compared to a McLeod gage using hydrogen in a static system. A 1-mm. differential on the oil gage corresponded to 0.06 mm. of mercury. Thus a pressure difference of 0.0006 mm. of mercury could be detected. The diffusion gage required about two minutes to come to equilibrium after small pressure changes.

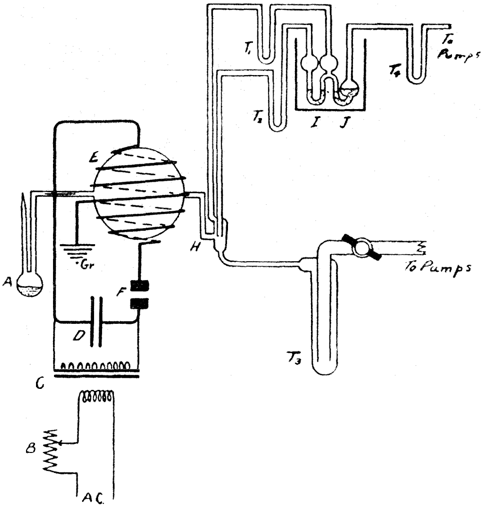

Fig. 1.

The gages were kept in a bath of oil to reduce temperature variations. Oil vapors were kept out of the rest of the apparatus by means of the traps T_1 and T_2 which were kept in a carbon dioxide–acetone mixture. At first the orifice chamber was cooled by an air blast, later it was placed in a thermostat.

The glow discharge was obtained from very low pressures up to about 1 mm. At the lower pressures the glow spread throughout the bulb and was of a bright greenish-blue color. The discharge would not start itself at a pressure above about 0.6 mm., but once started, it continued to operate until an upper limit was reached at about 1 mm. At the higher pressures the discharge took on a ring form.

The degree of dissociation measured by the diffusion gage increased with the chlorine flow. In the range of 5 to 10 cc. per minute generally used here this change was small. With chlorine pressures between 0.2 and 0.7 mm., the degree of dissociation varied between about 0.08 and 0.18, tending to decrease at the higher pressures. When the temperature of the orifice chamber and leads was varied from −80 to 100° the dissociation increased from 0.04 to 0.09. This change was probably due to the more rapid motion of the gas at the higher temperature.

After a few hours of operation the discharge bulb became coated with a white

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(3) Wrede, *Z. Physik*, 64, 51 (1929).

deposit. After a longer time the connecting tubes showed a similar deposit. When the bulb was cooled by a blast of air less of this material formed. It was found to sublime slowly when heated to redness in air. It was insoluble in water and the common acids. The degree of dissociation did not change greatly with time, showing that the deposit had little activity for the recombination of chlorine atoms.

Properties of **Atomic** Chlorine.—To obtain some information concerning the catalytic activity of materials for the combination of the atoms, the method which Bonhoeffer[2] used with atomic hydrogen was chosen. The method consists of coating the materials on the bulb of a thermometer placed in the active gas and observing the temperature rise. The apparatus was similar to that used above, except that the Wrede gage was replaced by a tube to contain the thermometer. The bulb of the thermometer was directly in the gas stream about 7 cm. from the discharge bulb. The materials were either placed directly on the bulb or on a thin glass cap which fitted closely over it. The apparatus was cooled by an air blast. The results are shown in Table I.

TABLE I

CATALYTIC ACTIVITY IN CHLORINE RECOMBINATION

Material	Maximum temperature, °C.	Material	Maximum temperature, °C
Pyrex glass	30	NaCl, fused	34
Ag foil	115+	KCl, fused	70
Cu foil	115+	AgCl, fused	91
Al foil	82	$CaCl_2$, fused	66
Ni wire	120	$CoCl_2$, evap.	72
Platinized glass	35	Gas carbon	115+

The silver and copper were rapidly attacked, forming an adherent layer of chloride. The aluminum and nickel showed no sign of attack. Sodium chloride, potassium chloride and platinum were erratic in behavior, some samples heated rapidly, others not at all. Their activity was always lost after running for some time.

The pressure difference produced at the diffusion gage and the heating effect produced with some materials showed conclusively that we produced chlorine atoms and not more complex molecules. Since chlorine attacks silica at high temperatures to produce silicon tetrachloride it is not surprising that the atoms attack glass at moderate temperatures. The products would of course be different. The deposit observed could not have been one of the normal chlorides of silicon or boron since these are quite volatile.

The fact that the atoms can pass through a tube at a temperature much below the normal boiling point for the liquid is very unusual. Hydrogen, oxygen and nitrogen atoms are all condensed when passed into a liquid air trap, This difference in behavior may be due to the fact that these latter gases need a certain water content to prevent recombination while chlorine does not. If water had been required with chlorine the study of its reaction with hydrogen would have been made difficult if not impossible.

The data obtained with catalysts for the recombination showed which materials should be avoided in order to reduce recombination, and which may be used to aid recombination. Thus silver was chosen for use in the diffusion gage and for stopping the reaction. Silver, copper, nickel, carbon and similar materials were carefully excluded from the rest of the apparatus.

The recombination on glass, sodium chloride, potassium chloride and platinum was small, but the method was not sensitive enough to distinguish between them in activity. The initial activity observed with platinum, sodium chloride and potassium chloride may have been due to impurities which later volatilized. The low activity of platinum and sodium chloride agrees with the results of Senftleben and Polanyi.[4]

Silver should be a good material for detecting chlorine atoms in a molecular ray or elsewhere. Their action on a thin mirror surface was particularly noticeable. The mirror remained bright on the glass side for several days when exposed to dry chlorine, but immediately turned white and translucent when treated with atomic chlorine.

In view of the great catalytic activity of copper it seems remarkable that Jost and Sweitzer[6] were able to pass activated chlorine through a copper capillary while Bodenstein and Taylor[a] and others were unable to pass it through glass capillaries at somewhat smaller velocities.

The Reaction of Chlorine Atoms with Hydrogen.—The apparatus used is shown in Fig. 2. It consisted of a chlorine supply, A, a hydrogen leak, F, the discharge bulb, B, Wrede gage, C, with oil manometers G and H, reaction tube, D, and the sampling train of liquid air traps T_6 to T_{11}. Traps T_6, T_7 and T_{12} were made with ground joints.

The chlorine bulb was kept in a large Dewar half filled with ethyl acetate at its melting point. A metal tube was provided for cooling with liquid air. The mixture was thoroughly agitated by a screw stirrer. A toluene thermometer was used to observe the temperature, which could be kept between -83.5 and $-84.0°$. Mixtures of carbon dioxide with alcohol or acetone were found unsatisfactory as they became several degrees cooler when chlorine was used, due to the heat absorbed by vaporization.

The hydrogen was taken from a commercial cylinder. It was bubbled through water into a gas buret which was used to measure the rate of flow. The flow was regulated by the capillary leak, F. Moisture was removed by trap T^1 which was immersed in liquid air.

The discharge bulb and coil circuit were of the same type as described above. The arrangement of the reaction tube and diffusion gage was changed with the different experiments and will be described later. They

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(4) Senftleben, Z. *Physik*, 32, **922 (1925)**; Polanyi and Bogdandy, Z. *Electrochem.*, 33, *554* **(1927)**.

(5) Jost and Sweitzer, *Z physik. Chem.*, **13B**, *373* **(1931)**.

(6) Bodenstein and Taylor, *Z. Electrochem.*, **22**, *202* **(1916)**.

were placed in a small thermostat which was controlled to 0.1°. A catalyst of silver foil was used in the gage for the recombination of chlorine atoms.

The connection used to lead the chlorine into the reaction tube was adjusted to the chlorine flow to prevent the diffusion of hydrogen back into it. When the total pressure was about 0.4 mm. and the tube was small enough to cause a pressure drop of about 0.1 mm. between the discharge bulb and the reaction tube no diffusion took place. This was shown by the fact that the spectrum of the discharge was not changed when the hydrogen flow was started The degree of dissociation also remained the same. Since the discharge could not be maintained at a pressure much above 1 mm. and the diffusion gage required a pressure of 0.5 mm. or less, the method was applicable only within the pressure range of 0.3 to 0.5 mm.

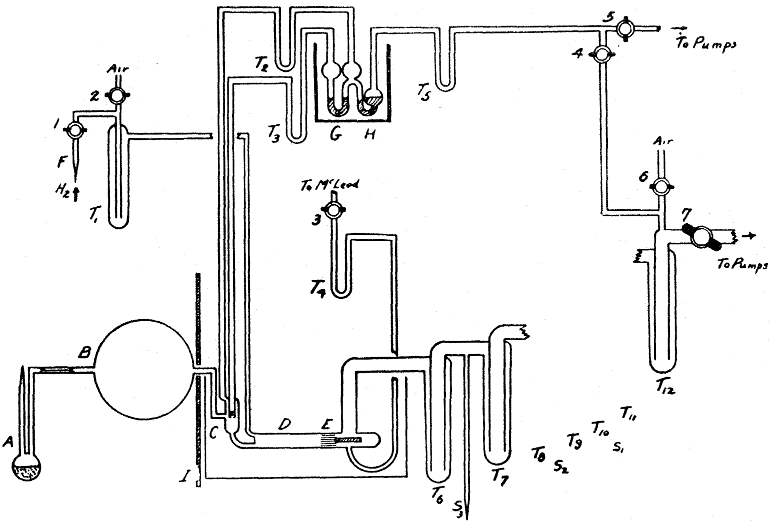

Fig. 2.

No sealing wax was used in the construction of the apparatus and the reaction mixture was protected from stopcock grease by liquid air traps.

Samples of the products were taken by placing Dewar flasks of liquid air on the sampling traps. The time of sampling, which was usually five or ten minutes, was terminated by placing liquid air on the next trap to the left. Conditions could then be changed and another sample taken.

When all the samples were taken, the discharge was turned off, and the pumps and hydrogen shut off. The samples were swept out one at a time through the sampling tubes after removing the liquid air from the corresponding traps. The chlorine and hydrogen chloride were absorbed in 200 cc. of 5% potassium iodide solution. Several tests showed that this procedure removed all of the chlorine and hydrogen chloride from the trap. The air flowing from both sides prevented the diffusion of the chlorine or hydrogen chloride into the other traps which were still cooled with liquid air.

The samples were analyzed by titrating with 0.20 *N* sodium thiosulfate without an indicator, then with 0.10 *N* potassium hydroxide using methyl orange indicator. All of the solutions were made from conductivity water which was also used in rinsing. Numerous blank runs were made to check the neutrality of the solutions and of the chlorine.

Extent of Reaction.—A reaction bulb of about 35 cc. volume was used. The diffusion gage was sealed directly into one side of the reaction bulb. It was connected to the discharge bulb by 7 cm. of 4 mm. tubing bent twice at right angles. The dissociation was measured at the beginning of each run before the hydrogen flow was started. The reaction was probably not confined to the reaction bulb, but also took place in the connecting tubes to the sampling traps which were at room temperature. The results are shown in Table II, the temperature given is that of the thermostat. The pressure was 0.4 mm. and the hydrogen flow 17.5 cc. per minute.

TABLE II

EXTENT OF REACTION WITH HYDROGEN

Temp., °C.	Cl_2, cc./min.	Dissociation	Cl_2 reacting, %
0	7.0	0.20	52
36	10.4	.20	97
99	8.8	.20	96
0	7.5	.07	24
25	7.9	.07	83
50	8.4	.07	99

It was observed that when the reaction bulb was not placed in the thermostat it became hot. The reaction then ran nearly to completion even with a very low degree of dissociation.

When there was an excess of chlorine, the hydrogen was sometimes completely used up, as shown by the very slow pressure increase when the pumps were shut off. The results were the same when the room was darkened to prevent the occurrence of a photochemical reaction. Blank tests with hydrogen and chlorine, but with the discharge off, showed no hydrogen chloride formation in either a darkened or a light room.

No reaction was observed when the current was not great enough to form a glow in the discharge bulb. With this arrangement a weak static discharge took place in the connecting tubes, but no dissociation could be detected by the gage.

Effect of Oxygen.—The same apparatus was used except that a bulb which had been silvered inside was placed after the reaction bulb. That it stopped the reaction beyond this point was shown by the fact that the silver was attacked only at the inlet. The hydrogen flow was 6.7 cc. per minute and a flow of 0.08 cc. per minute of oxygen was added to it by means of a capillary leak. The chlorine flow was about 9 cc. per minute. Its dissociation was measured before and after each run; the average was about 0.04. Samples were taken with the oxygen flow on and then with it turned off.

The average yields, expressed as percentage of the chlorine reacting, were: with oxygen 21% at 0° and 38% at 25°; without oxygen 25% at 0° and 36% at 25°.

Effect of Surface.—The effect of surface was studied using an empty Pyrex bulb of about 60 cc. volume, and the same bulb filled with short lengths of 4-mm. Pyrex tubing. The surface to volume ratio was changed from 2 to 10. The apparatus was thoroughly cleaned with hot $CrO_3 \cdot H_2SO_4$ The diffusion gage was arranged as in Fig. 2 and the chlorine was mixed with the hydrogen just at the inlet to the bulb. The dissociation was measured for each sample and was about 0.10.

The yields, calculated as the molecules of hydrogen chloride formed per chlorine atom introduced, were 3.1 and 5.0 at 0 and 25° for the packed bulb, and 2.8 and 3.8 at 0 and 25" for the empty bulb.

Rate of Reaction.—The apparatus is shown in Fig. 2. The light of the discharge was screened off by the shield I. The connecting tube from B to C was a 6 cm. length of 6 mm. tubing, that from C to D was a 1.5 cm. length of 4 mm. tubing. The reaction tube D was about 1.3 cm. wide and 8 cm. long and was calibrated from the inlet side. The system was made quite small in order to keep the amount of reaction small and the partial pressures of chlorine atoms and hydrogen nearly constant.

The reaction was stopped at the desired time by a roll of silver foil about 1 cm. wide shown at E. It caused all the atoms to recombine. A glass covered iron armature fastened to the silver foil made it possible to move it by means of a magnet and hence to vary the time of reaction.

The pressure of the reacting mixture was measured by a McLeod gage with a ratio of 875 to 1. The dissociation was measured twice for each sample and the readings were averaged. The time required for the chlorine to pass from the discharge bulb to the reaction tube was about 0.015 second.

Results.—When the silver foil was placed about 2 mm. from the inlet end of the reaction tube, the amount of reaction was very small. This showed that the foil was very effective in stopping the reaction and that no hydrogen was diffusing into the chlorine leads.

The data for a typical run are given below

Reaction volume	10 cc.
Hydrogen flow	6.3 cc. per minute
Pressure	0.340 mm. of mercury
Time of sampling	10 minutes
Reaction temperature	0.0°
Temperature of chlorine	−83.5°
Total pressure at diffusion gage	7.00 mm. of oil

Differential pressure across orifice	0.40 mm. of oil
Degree of dissociation of chlorine	0.11
Thiosulfate titration	36.5 cc. of 0 20 N
Potassium hydroxide titration	9.1 cc. per minute
Chlorine flow	9 1 cc. per minute
Per cent. of chlorine reacted	10.2
Hydrogen chloride formed per Cl atom introduced	0.92
Time of reaction	0.016 seconds
Number of collisions per Cl atom	30 X 10^3
Probability for reaction	1 5 X 10^{-5}

The last two entries were calculated by the kinetic theory. The number of collisions, Z, which a molecule of type I (Cl) makes with molecules of type II (H_2) per second is

$$2N_2\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{m_1+m_2}{m_1m_2}}\sqrt{2\pi kT}$$

N_2 is the number of type II molecules in volume V, d_1 and d_2 are the collision diameters, and m_1 and m_2 are the corresponding masses. The diameter of the chlorine atom is not known. The value given for argon ($d = 2.97 \times 10^{-8}$)[7] was used. The value for hydrogen ($d = 2.39 \times 10^{-8}$) was taken from the same source.

The average number of collisions, Z', which a chlorine atom experienced while in the reaction tube is

$$Z' = Z\, nV_R/N_T$$

Where n is the total number of molecules per cc. in the reaction tube of volume V_R, and N_T is the total number of molecules entering the tube per second.

It was assumed that the reactions involved were

$$Cl + H_2 = HCl + H \qquad (I)$$
$$H + Cl_2 = HCl + Cl \qquad (II)$$

and that the rate of (II) was greater than the rate of (I). Thus each chlorine atom which reacted would form 2HCl. The ratio of HCl formed to the Cl introduced was found by dividing the fraction of chlorine which reacted by the degree of dissociation.

The probability, W, of a chlorine atom reacting with a hydrogen molecule on collision is

$$W = (HCl/Cl)/2Z'$$

The results of the other rate measurements are shown in Table III. The temperature is in degrees centigrade, pressure in mm. of mercury, and reaction volume in cc. The values in the columns headed H_2 and Cl_2 are the corresponding rates of flow in cc. at N. T. P. per minute. The degree of dissociation of the chlorine (a) is given in column 6. Column 8 gives the yield of HCI per chlorine atom calculated from the dissociation

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(7) "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, p. 249.

and the amount of HCl formed. Column 9 gives the number of collisions (Z') one chlorine atom had with hydrogen molecules in passing through the reaction tube. The probability (W) of a chlorine atom reacting with hydrogen on collision is given in column 10.

TABLE III

RATE OF REACTION OF ATOMIC CHLORINE WITH HYDROGEN

Test	T	P	V	H_2	a	Cl_2	HCl/Cl	$Z' \times 10^{-3}$	$W \times 10^5$
I	0.0	0.30	9.3	6.6	0 049	9.8	0.57	21	1.4
2	.0	.30	9.3	6.6	042	10.1	.62	21	1.5
3	.0	.30	9.7	6.6	.050	9.2	.62	24	1.3
4	.0	.30	9.7	6.6	,050	9.0	.64	26	1.2
5	.0	.31	9.7	6.3	050	9.4	62	25	1.2
6	.0	.29	4.8	6.3	.056	9.6	.23	10	1.2
7	.0	.28	4.8	6.3	.062	10.1	30	9.2	1.6
8	.0	.30	9.7	6.3	.065	10.0	.58	21	1.4
9	25	.27	9.4	6.4	.110	9.7	93	14	3.3
10	25	.27	4.8	6.4	.110	9.5	59	7.6	3.8
11	25	.28	4.8	6.7	.070	9.7	47	8.5	2.8
12	25	.30	9.7	6.7	.066	9.2	1.05	21	2.5
13	25	.29	9.7	6.6	.090	9.7	0.78	18	2.2
14	25	.28	9.7	6.6	.087	10.2	.75	16	2.3
15	0.0	.32	9.7	6.6	.048	9.7	.40	26	0.8
16	.0	.32	9.7	6.6	.051	9.0	.46	27	.8
17	.0	.34	10	6.3	.110	9.1	.92	30	1.5
18	.0	.33	10	6.3	.110	9.4	90	27	1.7
19	25	.30	10	6.3	.20	8.2	1.43	21	3.4
20	25	.31	5.0	6.4	.114	9.4	0.55	10	2.8
21	25	.32	5.0	6.4	.106	9.7	.47	11	2.1
22	0.0	.32	5.0	6.4	.077	10.7	.16	11	0.7
23	.0	.31	5.0	6.4	.070	10.7	.15	11	.7

The reaction tube was cleaned after test 12. A new reaction tube, orifice chamber and discharge bulb was placed in the apparatus before test 17.

Following these tests a glass plate was placed before the silver catalyst. The clearance around the edge of the plate was about 0.5 mm. and its presence caused a pressure drop of about 0.2 mm. It should have prevented a lowering of the concentration of atomic chlorine by diffusion to the catalyst. The yield was somewhat higher, but since the pressure was uncertain, the collisions could not be calculated.

A run was also made in which the hydrogen was saturated with water vapor at room temperature. There was slightly less reaction than with the dried gas. A maximum value for the water in the chlorine may be calculated from the vapor pressures. The vapor pressures of chlorine and ice at −80° are 58.7 mm. and 0.0004 mm., respectively. At the operating pressure this would give a partial pressure of water vapor of about 10^{-6} mm. Since the chlorine was dried before being liquefied this figure is probably much too high.

The saturated hydrogen contained about 3% water vapor. This would give a partial pressure of water vapor of about 0.003 mm. in the reaction tube, at least 3000 times that in the dry gases.

Discussion of the Chlorine–Hydrogen Reaction.—The reaction of chlorine with hydrogen has been the subject of so many studies that complete references cannot be given here.[8] The original mechanism proposed by Nernst is a chain involving two steps

$$Cl + H_2 = HCl + H \qquad (I)$$

$$H + Cl_2 = HCl + Cl \qquad (II)$$

It has been generally accepted that (2) takes place and that it is a rapid reaction Bodenstein has estimated a reaction probability of 10^{-3} per collision for (2). Most of the discussion has centered around (1). The question concerning this step in the reaction apparently was raised by the work of Coehn and Jung,[9] who claimed that a trace of water was necessary for the photochemical reaction. It seemed necessary to introduce water into the reaction mechanism somewhere and various proposals were made which involved replacing (1) by various complicated mechanisms.

The experiments reported above prove conclusively that the reaction

$$Cl + H_2 = HCl + H$$

does take place, at least at low pressures.

The completeness of the reaction, when allowed to run in a fairly large volume, shows that a chain reaction takes place. The chains are short, due to the large number of chlorine atoms introduced compared to the total reacting mixture. This fact also accounts for the lack of any effect of light on the yields The number of atoms which could be formed by light absorption under the experimental conditions would be very small compared to the number present.

The negligible effect of additional surface of Pyrex glass was due to its small activity for recombination of chlorine atoms. Since hydrogen atoms recombine rapidly on dry glass surfaces, this effect shows that either the hydrogen atoms react very rapidly with chlorine or that their recombination is prevented by a layer of chlorine adsorbed on the glass.

The absence of an appreciable retardation of the reaction by oxygen was due to the shortness of the chains. Photochemical work has shown that the effect of oxygen is very great when the chains are long, but small when the chains are short.

The largest source of error in measuring the rate of reaction was the recombination of the atoms on the walls. A clean glass surface was only slightly active, but the activity increased with the time of operation. This is shown in Table III by tests 9 to 14. The probability of reaction decreased from about 3.5×10^{-5} to about 2.3×10^{-5}. A similar decrease

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(8) For recent references see Bodenstein, *Trans. Faraday Soc.*, 27, 413 (1913); Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co , New York, 1932

(9) Coehn and Jung, *Z. physik Chem.*, 110, 705 (1924)

is shown by tests 17 to 23. When the reaction tube was kept at 0° all the time the discharge was on, this change was slow. This indicates that some of the material which sublimed from the discharge bulb may have deposited on the walls and increased the atom recombination.

At the lower temperature less of this material could have reached the reaction bulb because of better condensation in the lead tubes.

Another possibility of error was the diffusion of the atoms to the silver catalyst. This would lower the concentration of chlorine atoms in the reacting mixture and make the probability of reaction too low. The experiment with the glass plate for preventing diffusion showed that this effect was not very large. Tests 5 to 12 show that the amount of reaction was nearly proportional to the reaction volume. If the diffusion had been rapid, the amount of reaction should have increased more rapidly than the reaction.

The error in determining the degree of dissociation was about 5%. The rates of flow were known to about 2%. Titration errors of 5% are probable in the amount of hydrogen chloride formed. The total error for all measurements was about 10%.

Allowing for the decrease of reaction with time, the most reasonable values for the probability of reaction on collision are 1.4×10^{-5} at 0° and 3.3×10^{-5} at 25°. The reaction was carried out under conditions in which practically the only moisture present was that coming from the glass, thus approaching the conditions of dryness obtained in the experiments of Coehn and Jung.[9] The fact that no difference in the reaction was observed when moisture was present throws grave doubt upon their results and makes it unnecessary to speculate upon a mechanism involving the water molecule. This is in agreement with recent work by Bodenstein,[10] who has been unable to confirm the previous work upon the necessity of moisture to the reaction

Reaction Probability Calculated from the Results of Other Workers.—The photochemical rate of reaction experiment as ordinarily carried out at high pressures with constant illumination upon mixtures of hydrogen and chlorine is a measurement of average chain length only. Since the chain involves at least two alternating mechanisms and the average chain length depends upon the competition of these mechanisms with others, such measurements do not give direct information of reaction probability, heat of activation or any other fundamental property of the reaction. By making a sufficient number of assumptions, however, a figure may be arrived at and calculations have been made by several. The figures obtained vary from 10^{-3} to 10^{-6} for the mechanism (I). The value arrived at by Bodenstein[10] 10^{-4} is in approximate agreement with our result.

It must not be forgotten that in our calculation we assumed mechanism

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(10) Private communication.

(II) to be rapid so that two molecules of hydrogen chloride will be formed for each atom of chlorine. If this assumption were not true, the order of magnitude of the reaction probability would be unchanged.

The Heat of Activation of the Reaction.—$Cl + H_2 = HCl + H$ (I). It was assumed formerly that an exothermic reaction of the type of (I) required no heat of activation. This assumption is certainly not correct. The above reaction is probably exothermic but so long as the heat of reaction is less than the heat of activation it is not of great importance what the sign of the former is. We shall assume that reaction may take place only when the relative velocity in collision exceeds a certain critical value. This is equivalent to assuming that the activation energy is entirely in the form of kinetic energy of translation. Even when the critical energy is exceeded it is not likely that a collision will always result in reaction. Hence we introduce a "steric" factor. The reaction probability f is therefore given by an expression of the form[11]

$$f = K\left(\frac{1 + E_0}{RT}\right) e^{-E_0/RT}$$

where K the steric factor is presumably independent of temperature. From the ratio of the reaction probabilities at two temperatures we may calculate the value for the activation energy E_0. The average values obtained for the reaction probabilities at 0 and 25° give a value for E_0 of 6100 cal. The steric factor corresponding to this activation energy is 0.08, but because of the uncertainty of the experimental results only the order of magnitude may be established. The value of E_0, on the other hand, would not vary by more than 1000–2000 calories for the different reasonable combinations of individual results at the two temperatures.

It is interesting to compare these results with estimates that have been made by others as to the heat of activation. Rollefson and Lindquist[12] were led by a study of the photochemical reaction of iodine monochloride and hydrogen to postulate that only Cl atoms in the $^2P_{\frac{1}{2}}$ state react with molecular hydrogen. The $^2P_{\frac{1}{2}}$ state has an energy of about 2500 calories greater than the normal state. It would therefore be necessary to postulate an additional critical energy of collision of about 3500 calories to bring about reaction. On account of the large number of collisions which a chlorine atom undergoes on the average before it reacts with a hydrogen molecule, it seems probable that statistical equilibrium would be established between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states so that the same results should be obtained regardless of the original state of the chlorine atom. In Rollefson and Lindquist's experiments apparently the chlorine atoms reacted with something else much more readily than with hydrogen. Their postulate

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[11] Ref. 7, p. 987. The expression given above assumes the total energy of collision to be available for reaction. This is probably not a proper assumption but the value obtained for the heat of activation would not be greatly different in any case. The question will be discussed by one of the authors elsewhere.

[12] Rollefson and Lindquist, THIS JOURNAL, 52, 2793 (1930).

that only the $^2P_{\frac{1}{2}}$ state reacts with hydrogen is therefore not required by the evidence.

Eyring[13] has calculated the heat of activation of reaction (I) from wave mechanics and obtains a value for E_0 between 14,000 and 25,000 calories according to the assumptions. The agreement is perhaps as good as is to be anticipated.

The authors wish to express their appreciation to Professor Bodenstein for his courtesy in communicating to them his recent experimental results.

Summary

The technique of preparing chlorine atoms has been developed. The conditions favoring recombination of chlorine atoms are not the same as for hydrogen atoms.

When chlorine atoms are introduced into a hydrogen–chlorine mixture at low pressure a chain reaction is started which will run, under favorable conditions, until one of the gases is used up. Oxygen and water are without effect on this reaction and the simple mechanism proposed by Nernst is adequate to account for it.

The reaction probability for the reaction $Cl + H_2 = HCl + H$ (I) has been estimated to be 1.4×10^{-5} per collision at 0° and 3.3×10^{-5} at 25°. From the temperature coefficient a heat of activation of 6100 ± 1000 calories is estimated.

[13] Eyring, THIS JOURNAL, **53**, 2537 (1931).

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

The Photochemical Oxidation of Phosgene

BY G. K. ROLLEFSON AND C. W. MONTGOMERY

The direct photochemical oxidation of phosgene has never been reported in the literature. It was thought possible that the reaction might take place upon insolation with light of $\lambda < 2700$ Å., since Henri[1] had found evidence of predissociation of phosgene beginning in this region. The primary act of absorption is believed[2,3] to lead to the process

$$COCl_2 + h\nu \longrightarrow COCl + Cl$$

in which the intermediate compound COCl is formed. This same intermediate has been postulated in the mechanisms of Bodenstein, Lenher and Wagner[4] and Lenher and Rollefson[5] for the photochemical formation of phosgene.

[1] Henri, *Proc. Roy. Soc.*, (London) **A128**, 178 (1930).

[2] Almasy and Wagner-Jauregg, *Naturwissenschaften*, 19, 270 (1931).

[3] Herzberg, *Ergebnisse exakt. Naturwiss.*, *10*, 207 (1931).

[4] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **3B**, 459 (1929)

[5] Lenher and Rollefson, THIS JOURNAL. **52**, 500 (1930).

The direct oxidation has been found to take place upon irradiation with ultraviolet light. Since there can be but little question as to the direct formation of $COCl$ in the primary process, a study of the reaction must be chiefly concerned with the subsequent processes involving the intermediate. Thus an entirely new point of attack on the mechanism of phosgene photochemical reactions is afforded.

Experimental

The reaction vessels employed were of clear fused quartz, one a spherical bulb of about 200 cc. volume, the other a cylindrical absorption cell 20 cm. long and 2 cm. in diameter. The cylindrical vessel was mounted on end and illuminated from a source parallel to the longitudinal axis The source of illumination was the full light of the quartz mercury arc. Two Cooper-Hewitt quartz arcs were used, the earlier work being done with a 110-volt arc while later a 220-volt arc giving greater intensity in the ultraviolet was used. As the arc was run quite close to the reaction vessel, it was found necessary to cool the latter during the work at room temperature. This was done by allowing water to flow smoothly over the surface of the vessel. The temperature of the water never varied more than 2° over a run. For the work at 90 and 200°, a small electric oven having a long narrow quartz window was used. Temperature was kept constant at 90 * 2° and 200 * 3° by varying a slide wire resistance in series with the oven.

The phosgene (Kahlhaum) was distilled directly into the line from a glass bomb after freezing the liquid by means of liquid air. The phosgene was then distilled through three reservoir traps in the line, the gas being allowed to bubble through the liquid. Finally, approximately the first and last thirds were pumped off, the middle third being collected in a reservoir trap which was always kept immersed in a Dewar filled with ice water The liquid phosgene remained perfectly clear, showing no trace of discoloration. When the gas was needed, the liquid in the reservoir was allowed to vaporize into a three-liter bulb from which small amounts could be drawn. The chlorine was prepared by heating anhydrous cupric chloride in the manner previously described.[6,7] Oxygen was prepared electrolytically from potassium hydroxide solution, freed from hydrogen by passing over hot copper oxide, and dried in a storage tube containing magnesium perchlorate.

The course of the reaction was followed by measuring the pressure increase with time. For the low pressure work a sulfuric acid (sp. gr. 1.84) manometer was used and later, with higher pressures, mercury was used as the manometer liquid, protected by 3 or 4 cm. of sulfuric acid. Readings were taken with the arc off at intervals of fifteen to sixty minutes depending on the speed of the reaction. In several of the runs, in order to check the pressure readings, the oxygen was measured by freezing out the other gases (phosgene, carbon dioxide and chlorine) with liquid air.

Results

In Fig. 1 log ($COCl_2$) is plotted against time for several runs. The straight lines obtained indicate that the rate of reaction is proportional to the first power of the phosgene concentration.

The effect of incident light intensity was investigated by using various wire screens which had been previously calibrated by means of a thermopile. The results summarized in Fig. 2 show that the rate is proportional

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(6) **Rollefson, THIS JOURNAL, 51, 770 (1929).**

(7) **Loeb, *Phys. Rev.*, 35, 184 (1930).**

to the first power of the incident intensity. The intensity with no screen is taken as unity.

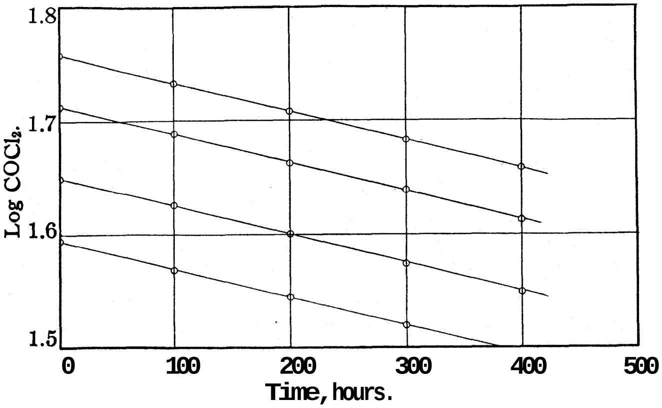

Fig. 1.

At higher oxygen pressures, the rate was found to be independent of the oxygen concentration, while at lower pressures, the rate gradually fell off with decreasing oxygen. This suggested that the rate of reaction might be a function of the chlorine-oxygen ratio rather than of the oxygen concentration itself. In Fig. 3 the rate is plotted against the function $1/(1 + k'(Cl_2/O_2))$ for the temperature, 90°. In each case such a value of k' was taken as would yield a straight line through the origin.

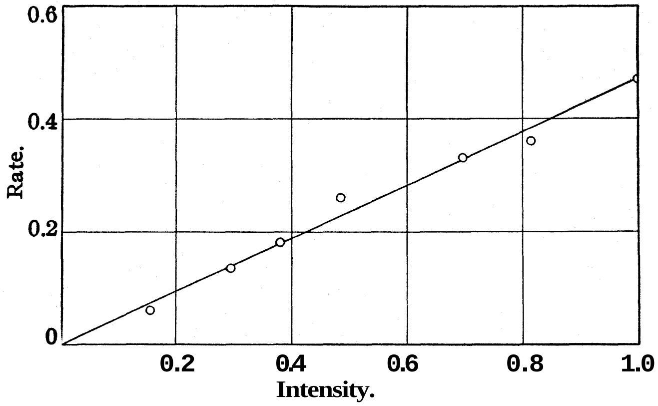

Fig. 2.

As has been pointed out[8] k' should be a definite function of the temperature. The reaction was therefore studied at three temperatures: 20, 90 and 200°. The values of K' found corresponding to these temperatures are as follows

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(8) Rollefson, This Journal. 55, 148 (1933).

Temp., °C.	20	90	200
K'	0.17	0.38	1.00

As an example of the data, the following values of the rate and the Cl_2/O_2 ratio may be given. These points are those obtained at 90° and are represented graphically in Fig. 3.

Rate	0.545	0.475	0.389	0.335	0.139
Cl_2/O_2	0.134	0.565	1.28	2.18	9.89
$1/[1 + 0.4(Cl_2/O_2)]$	0.95	0.81	0.66	0.53	0.22

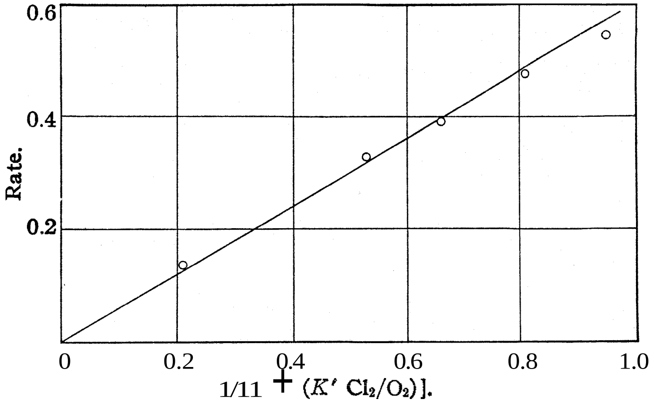

Fig. 3.

Discussion

The data presented above indicate that the rate law for the oxidation of phosgene may be expressed by the equation

$$\frac{d\,(CO_2)}{d\,t} = \frac{k\,I_0\,(COCl_2)\,(O_2)}{(O_2) + k'\,(Cl_2)}$$

or, showing more clearly the dependence on the chlorine-oxygen ratio

$$\frac{d\,(CO_2)}{d\,t} = \frac{k\,I_0\,(COCl_2)}{1 + k'\left(\frac{Cl_2}{O_2}\right)}$$

This rate law may be very simply derived from the following rate mechanism

$$\begin{array}{lll}
COCl_2 + h\nu & \longrightarrow COCl + Cl & (1) \\
COCl + O_2 & \longrightarrow CO_2 + ClO & (2) \\
COCl_2 + ClO & \longrightarrow CO_2 + Cl_2 + Cl & (3) \\
COCl + Cl_2 & \longrightarrow COCl_2 + Cl & (4) \\
Cl + W & \longrightarrow {}^1/_2Cl_2 + W \left.\right\} & (5a) \\
Cl + Cl & \longrightarrow Cl_2 & (5b)
\end{array}$$

Assuming that the rate of change of (COCl) and (ClO) is negligibly small compared to their rates of formation and reaction, we may write

$$\frac{d\,(\mathrm{COCl})}{d\,t} = I_{\mathrm{abs.}} - k_2\,(\mathrm{COCl})(\mathrm{O_2}) - k_4\,(\mathrm{COCl})(\mathrm{Cl_2}) = 0 \qquad (\mathrm{I})$$

$$\frac{d\,(\mathrm{ClO})}{d\,t} = k_2\,(\mathrm{COCl})(\mathrm{O_2}) - k_3\,(\mathrm{ClO})\,(\mathrm{COCl_2}) = 0 \qquad (\mathrm{II})$$

The rate of oxidation is given by

$$\frac{d\,(\mathrm{CO_2})}{d\,t} = k_2\,(\mathrm{COCl})(\mathrm{O_2}) + k_3\,(\mathrm{ClO})\,(\mathrm{COCl_2}) \qquad (\mathrm{III})$$

According to II we may write

$$k_3\,(\mathrm{ClO})(\mathrm{COCl_2}) = k_2\,(\mathrm{COCl})(\mathrm{O_2})$$

Substituting this expression in III, we obtain

$$\frac{d\,(\mathrm{CO_2})}{d\,t} = 2\,k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) \qquad (\mathrm{IV})$$

From I we have

$$k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) + k_4\,(\mathrm{COCl})\,(\mathrm{Cl_2}) = I_{\mathrm{abs.}}$$

$$\mathrm{COCl}\,(k_2\mathrm{O_2} + k_4\mathrm{Cl_2}) = I_{\mathrm{abs.}}$$

$$(\mathrm{COCl}) = \frac{I_{\mathrm{abs.}}}{k_2\mathrm{O_2} + k_4\mathrm{Cl_2}} \qquad (\mathrm{V})$$

Substituting V in IV gives us

$$\frac{d\,(\mathrm{CO_2})}{d\,t} = \frac{2\,k_2\,(\mathrm{O_2})\,I_{\mathrm{abs.}}}{k_2\mathrm{O_2} + k_4\mathrm{Cl_2}} \qquad (\mathrm{VI})$$

Since the total amount of light absorbed is small, we may write

$$I_{\mathrm{abs.}} = I_0\,(\mathrm{COCl_2})$$

which reduces VI to the expression already obtained experimentally

$$\frac{d\,(\mathrm{CO_2})}{d\,t} = \frac{2\,I_0\,(\mathrm{COCl_2})\,(\mathrm{O_2})}{(\mathrm{O_2}) + (k_4/k_2)\,(\mathrm{Cl_2})} = \frac{kI_0\,(\mathrm{COCl_2})\,(\mathrm{O_2})}{(\mathrm{O_2}) + k'\,(\mathrm{Cl_2})}$$

As (Cl) does not enter the derivation explicitly, it is immaterial which process (5a or b) leads to recombination. The rate mechanism is seen to lead to a quantum yield of 2, a point which is to be tested experimentally in the near future.[9]

The manner in which oxygen and chlorine enter the rate law brings out once more the close analogy between a purely chemical process in which two reactants ($\mathrm{Cl_2}$ and $\mathrm{O_2}$) are in competition for a chemical intermediate (COCl) and the process of quenching of fluorescence. This similarity which holds even to the form of the mathematical expressions involved may be seen clearly in this case. Here, although we do not have fluorescence, we may say that the COCl molecule has a definite life period with respect to its reaction with chlorine. If, however, we start with a definite chlorine pressure and vary the oxygen pressure, the number of COCl molecules formed which react with chlorine will decrease as the oxygen pressure

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(9) Experimental evidence obtained from a comparison with the phosgene sensitized formation of carbon dioxide which is very similar to the chlorine sensitized reaction indicates that the quantum yield cannot be greater than 10 and is probably of the order of magnitude of 2 or 3. This phosgene sensitized reaction is being investigated in this Laboratory and the results will be published in the near future.

increases in much the same manner that the intensity of fluorescence decreases with increasing amount of foreign gas present.

k' has been shown to be equal to the ratio k_4/k_2 and may thus be interpreted as a measure of the relative reactivity of chlorine and oxygen with COCl. These two reactions (2 and 4) also appear in the mechanism proposed by Lenher and Rollefson.[5] In some recent work, Rollefson[8] has studied the relative amounts of carbon dioxide and phosgene produced by these two processes in the chlorine sensitized oxidation of carbon monoxide. In both this reaction and the direct oxidation, the same intermediate COCl is reached, though by entirely different processes. Likewise, in both reactions, COCl is believed to react in the same manner with oxygen and chlorine. This parallelism between the two systems is emphasized by the plot in Fig. 2 of Rollefson's paper which shows that the relative efficiencies of oxygen and chlorine are the same for both reactions at all temperatures. While it is possible that different intermediates might give the same ratio at one temperature, it is extremely improbable that the temperature coefficients would also be the same. Therefore we believe that the experiments presented here constitute a definite proof of the existence of COCl as an intermediate in the reactions discussed.

Summary

The direct photochemical oxidation of phosgene has been studied and the following rate law has been determined for the reaction

$$\frac{d(CO_2)}{dt} = \frac{k I_0 (COCl_2)(O_2)}{(O_2) + k'(Cl_2)}$$

A mechanism has been suggested for the reaction and the results have been correlated with the work of Lenher and Rollefson on the photochemical formation of phosgene and the chlorine sensitized oxidation of carbon monoxide.

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

The Photochemistry of Mixtures of Chlorine, Oxygen and Carbon Monoxide

BY G. K. ROLLEFSON

When mixtures of carbon monoxide, chlorine, and oxygen are illuminated with light which is absorbed by the chlorine, part of the carbon monoxide is changed to phosgene and part to carbon dioxide. At relatively high pressures of oxygen, carbon dioxide formation occurs almost exclusively, whereas at low oxygen pressures the phosgene formation is predominant. The action of oxygen in this system has been attributed to a reaction with the intermediate COCl.[1,2] According to the mechanism of Lenher and Rollefson the COCl molecule may react either with chlorine or oxygen, the relative amounts of the two being determined by the specific rate constants for the reactions and the relative pressures of the two gases. In the original mechanism of Bodenstein, Lenher and Wagner it was postulated that only the oxygen reacted with the COCl and the latter compound was assumed to be in equilibrium with carbon monoxide and chlorine in the absence of oxygen but not in the presence of oxygen. Recent work from Bodenstein's laboratory[3] indicates that they now accept the view held by Lenher and Rollefson that COCl reacts with both oxygen and chlorine, but they still retain the assumption of equilibrium in the absence of oxygen and a non-equilibrium state in the presence of oxygen. In order to have such conditions it is necessary that the rates of formation and decomposition of COCl be fast compared to the rate of reaction of COCl with chlorine and comparable with the rate of oxidation of COCl. It is the purpose of this paper to present experimental results which show that the specific rates for the reactions of COCl with chlorine and oxygen are of the same order of magnitude and therefore the postulates of Bodenstein and his students are invalid.

The experimental procedure for determining the relative efficiency of reaction of chlorine and oxygen with COCl is suggested by a comparison with the most simple system of this type which we can find, namely, the quenching of fluorescence by the addition of gases. In that case we may represent the processes involved by the equations

$$A^* = A + h\nu$$
$$A^* + M = A + M + \text{kinetic energy or } A + M^* + \text{kinetic energy}$$

That is, we have the activated molecules, A, returning to the normal state with the emission of light or being deactivated by collision with some molecule M. The relative-amounts of these two processes are well known from

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(1) Lenher and Rollefson, THIS JOURNAL, 52, 500 (1930).

(2) Bodenstein, Lenher and Wagner, Z. *physik.* Chem., B3, 459 (1929).

(3) Schumacher and Stieger, *ibid.*, B13, 157 (1931).

results in the literature. In the present case we do not have any fluorescence, but we may speak of the COCl molecule as having a certain life period with respect to its reaction with chlorine. Now if we take a definite pressure of chlorine and vary the pressure of the oxygen, the fraction of the total number of COCl molecules formed that react with chlorine will decrease as the oxygen pressure increases, much as the intensity of fluorescence is decreased by the addition of a foreign gas. To express this behavior in terms of chemical equations, let us consider the reactions

$$COCl + Cl_2 = COCl_2 + Cl \qquad (1)$$

$$COCl + O_2 = CO_2 + ClO \qquad (2)$$

The rates of these reactions are given by

$$-\frac{d\,(Cl_2)}{d\,t} = k_1\,(COCl)\,(Cl_2)$$

$$-\frac{d\,(O_2)}{d\,t} = k_2\,(COCl)\,(O_2)$$

The fraction of the phosgene molecules reacting with oxygen is

$$\frac{\dfrac{d\,(O_2)}{d\,t}}{\dfrac{d\,(O_2)}{d\,t} + \dfrac{d\,(Cl_2)}{d\,t}} = \frac{k_2\,(COCl)\,(O_2)}{k_1\,(COCl)\,(Cl_2) + k_2\,(COCl)\,(O_2)} = \frac{1}{1 + \dfrac{k_1}{k_2}\dfrac{(Cl_2)}{(O_2)}}$$

According to this equation the number of moles of oxygen reacting according to (2) will be equal to the number of moles of chlorine reacting according to (1) when $k_1(Cl_2)$ is equal to $k_2(O_2)$. Therefore if we determine the ratio of the pressures of chlorine and oxygen for which equal numbers of moles of these two gases react, we will have the ratio of the rate constants.

The experimental technique involved is extremely simple, consisting of illuminating mixtures of chlorine, oxygen and carbon monoxide and determining the extent of the two reactions from the pressure change at room temperature and also after freezing out the condensable gases with liquid air. In order to show how this is done, consider the two reactions

$$2\,CO + O_2 = 2\,CO_2$$

$$CO + Cl_2 = COCl_2$$

Let Δp_1 be the pressure change due to the first reaction and Δp_2 be that due to the second. The total pressure change is $\Delta p = \Delta p_1 + \Delta p_2$. One other equation involving Δp_1 and Δp_2 will suffice for the determination of these two quantities. To obtain this consider the changes in the sum of the carbon monoxide and O_2 pressures which we shall represent by $\Delta(CO + O_2)$.

$$\Delta(CO + O_2) = 3\Delta p_1 + \Delta p_2$$

Combining this with our previous equation

$$\Delta p_1 = {}^1/_2[\Delta(CO + O_2) - \Delta p]$$

$$\Delta p_2 = \Delta p - \Delta p_1$$

Since carbon dioxide, chlorine and phosgene all have very low vapor pressures at liquid air temperatures the pressure measured when the reaction vessel is immersed in liquid air is that of the carbon monoxide and oxygen. The value of $\Delta(CO + O_2)$ may be obtained by immersing the reaction vessel in liquid air before and after a period of illumination, reading the change in pressure, and calculating the value of $\Delta(CO + O_2)$ at room temperature by means of an experimentally determined factor. This factor varies slightly with temperature of the liquid air but was usually about **3.2.**

In Fig. 1 the values of $\Delta O_2/(\Delta O_2 + \Delta Cl_2)$ obtained at 20° are plotted against the values of Cl_2/O_2. From this curve we find that the number of moles of chlorine and oxygen reacting are equal when the chlorine pressure is 5.0 times that of the oxygen. In order to be certain that the relative amounts of the two reactions are a function solely of Cl_2/O_2, the partial pressures of the reactants were varied between the following limits (pressures in cm. of sulfuric acid): carbon monoxide from 10 to 25, chlorine from 18 to 57, oxygen from 2.7 to 42. Regardless of the pressures used the points fall on the curve within the limits shown by the graph, thereby justifying the assumption that the relative amounts of chlorine and oxygen reacting are a function solely of the ratio of these two gases.

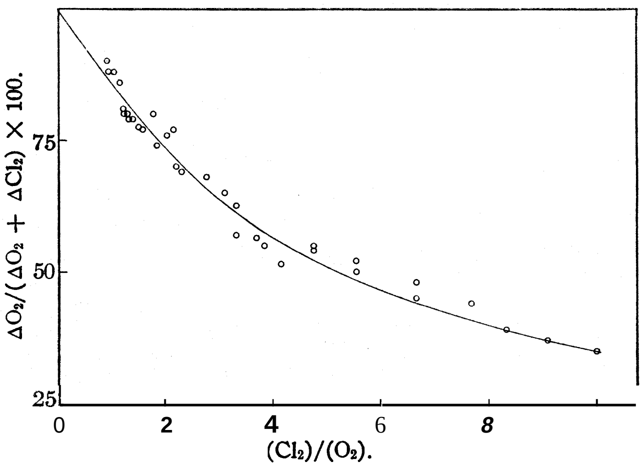

Fig. 1.

If we carry out experiments of the same type at different temperatures the division between reactions (1) and (2) should vary, as the heats of activation for the two reactions would normally be expected to be different. Such experiments have been carried out at 89 and 130°. The results fall on the same type of curve as those at 20° but the values of Cl_2/O_2 for which the rates of (1) and (2) are equal are 2.0 and 1.25, respectively. Such a trend shows that reaction (1) has a higher temperature coefficient and therefore a higher heat of activation than reaction (2). The difference between the heats of activation may be calculated from a consideration of the relationship existing between the rate constant and temperature,

$k = se^{-Q/RT}$, where s is a factor involving the number of collisions and possibly some steric factor, and Q is the heat of activation. If we let the subscripts 1 and 2 refer to the reactions (1) and (2) we have

$$\frac{k_1}{k_2} = \frac{s_1}{s_2} e^{-(Q_1 - Q_2)/RT}$$

Taking the logarithms of both sides

$$\ln \frac{k_1}{k_2} = \ln \frac{s_1}{s_2} - \frac{Q_1 - Q_2}{RT}$$

Therefore if we plot the logarithms of the experimentally determined values for k_1/k_2 against the reciprocal of the absolute temperature a straight line should be obtained. The slope of this line is $-(Q_1 - Q_2)/R$ and the intercept on the $\ln(k_1/k_2)$ axis is $\ln(s_1/s_2)$.) Figure 2 shows such a plot of the data reported in this paper combined with that obtained by Rollefson and Montgomery[4] using phosgene as a source of COCl. From the graph we find that $Q_1 - Q_2 = 2880$ cal. and $\ln(s_1/s_2) = 3.16$ or $s_1/s_2 = 24$. These figures are taken from the line which represents the combined results of the two researches; if the line is drawn through the points obtained by the method reported in this paper a slightly higher result, 3200 cal., is obtained for $Q_1 - Q_2$ and 38 for s_1/s_2. Due to the approximate methods of calculation used in obtaining k_1/k_2 in the work of Rollefson and Montgomery the higher values given above are favored. Probably the best values **are** 3000 ± 200 cal. for $Q_1 - Q_2$ and 30 ± 5 for s_1/s_2.

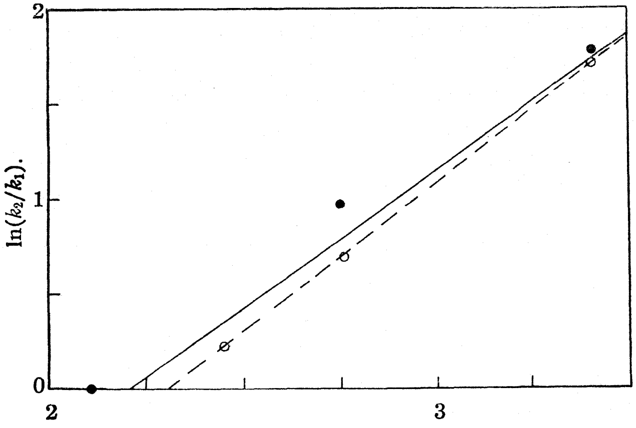

Fig. 2.

The interpretation of the difference in the two heats of activation must await an explanation of the nature of such activation. The s values, however, have been interpreted as collision numbers modified by a "steric" factor. In the case we are concerned with the difference in the number of

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(4) Rollefson and Montgomery, THIS JOURNAL, 55, 142 (1933)

collisions of COCl with oxygen and with chlorine cannot be very great. Using the data for molecular diameters obtained from viscosity measurements it may be calculated that if the same pressures of the two gases were used there would be 1.45 times as many collisions with chlorine as with oxygen. After allowing for this effect we have a factor of approximately twenty for the so-called "steric" effects. This does not mean that there are twenty times as many geometrical arrangements of COCl and Cl_2 which lead to reaction as there are of COCl and O_2, but rather the probability of a rearrangement to give the products is twenty times as great in the former case as in the latter. This difference in probabilities may be due in part to geometrical considerations but must depend also on such factors as changes in electron spins and electron distribution.

From the facts which have been presented we have a definite mechanism to account for the diminishing effect of oxygen as the temperature is raised. That COCl is an intermediate step in the formation both of carbon dioxide and phosgene seems very definitely established by the identity of the ratio of the rate constants obtained by the two methods of attack. Furthermore, the results indicate that CO_2 formation should not disappear entirely as the temperature is raised but should be small except in the presence of relatively high pressures of oxygen. From the magnitude of the ratios observed we see that at equal pressures of oxygen and chlorine the rates of reaction with COCl never differ by more than a factor of approximately five in the temperature range from 20 to 200°. This means that we can never consider either reaction as negligible compared to the other under comparable conditions and therefore Bodenstein's postulate that COCl is present in its equilibrium concentration in the phosgene reaction and not in the sensitized carbon dioxide formation must be considered extremely questionable. A more quantitative discussion of the magnitude of the rates of the individual steps in the mechanism must await the development of the mechanism for the chlorine sensitized photochemical formation of carbon dioxide.

Summary

An experimental investigation has been made of the relative amounts of carbon dioxide and phosgene formed when mixtures of carbon monoxide, chlorine and oxygen are illuminated with light absorbed by the chlorine. It has been shown that the relative amount of the two reactions is a function solely of the ratio of chlorine to oxygen provided the temperature is kept constant. If the temperature is varied the logarithm of the ratio is a linear function of the reciprocal of the absolute temperature. These facts have been shown to be in accord with the assumption that the carbon dioxide and phosgene are formed by the reaction of an intermediate compound COCl with oxygen and chlorine, respectively.

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Heat Capacity Curves of the Simpler Gases. I. Heat Capacity, Entropy and Free Energy of Gaseous Nitric Oxide from Near Zero Absolute to 5000°K.[1]

BY HERRICK L. JOHNSTON AND ALAN T. CHAPMAN

In carrying out various types of thermodynamic calculations, an accurate and assured knowledge of the heat capacities of the substances involved is often essential. Frequently, at least one of the constituents in such considerations is a gas and, due to inherent experimental difficulties, the literature is generally lacking in reliable values for the specific heats of gases.[2] The latter observation is particularly true for data taken either at very high or at very low temperatures. Yet, frequently, it is in these more extreme temperature regions that a more exact knowledge of the heat capacity curves assumes greatest interest and importance.

Moreover, until quite recently no adequate quantitative theory had been proposed to account for the heat capacities of molecules containing more than one atom. The most useful guide had been the principle of the Equipartition of Energy, enunciated by Boltzmann.[3] This principle was derived by application of statistical methods to a classical energy distribution among the various degrees of freedom associated with the translational, rotational and vibrational motions of the molecules. For monatomic gases the Equipartition Principle yields correct specific heats,[4] but its inadequacy to account correctly for the magnitudes, as well as the variations, in the specific heats of more complex gases constituted one of the original arguments in favor of quantum theory.

The approach to a correct solution of the more general problem was made, independently, by Kemble[5] and by Reiche.[6] These authors attempted to calculate the rotational portion of the heat capacity of hydrogen on the basis of what was then known concerning rotational quantization in molecules. By considering the diatomic molecule as a rigid rotator, Reiche obtained the well-known equation for C_R, the molar rotational heat capacity, which takes the form[7]

$$C_R = \sigma^2 R \frac{d^2 \ln Q}{d\sigma^2} \tag{1}$$

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[1] Presented March 31, 1931, as part of the Symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

[2] The low temperature measurements on hydrogen, made by Cornish and Eastman [THIS JOURNAL, 50, 627 (1928)] are a noteworthy exception.

[3] Boltzmann. *Sitzb. Akad. Wiss. Wien.*, 58 (1861).

[4] Except at high temperatures, where all monatomic gases will rise above the equipartition value due to electronic excitation.

[5] Kemble, *Phys. Rev.*, 11, 156 (1918).

[6] Reiche, *Ann. Physik*, 58, 657 (1919).

[7] Here R is the molar gas constant; T, the absolute temperature; k, the gas constant per molecule: I, the moment of inertia; p_m the statistical weight of the rotational state possessing the quantum number "m": and the summation is over all values of "m" from m_{minimum} to ∞.

$$\text{where } \mathbf{a} = \frac{h^2}{8\pi^2 IkT} \text{ and } Q = \Sigma_m p_m e^{-m^2\sigma}$$

There existed, at that time, considerable uncertainty both with respect to the proper choice of statistical weights and with respect to the value of "m" for the lower limit of the summation. These uncertainties have since been removed both through the recent advances in the wave mechanics and through progress in the empirical analysis and interpretation of molecular spectra. But working prior to these more recent developments, Reiche was limited by the dilemma of several alternative solutions for equation (1), which depended on the choice of values for "p_m" and "m." Out of some five alternatives, one solution yielded a specific heat curve whose shape was in rough agreement with the experimental curve for hydrogen. As we now know, the agreement would have been much improved had account been taken of the, then unsuspected, dual nature of molecular hydrogen.[8]

Urey[9] applied Reiche's treatment to the rotational heat capacities of several diatomic and a few polyatomic molecules. This treatment still involved the assumed condition of rigid rotators but represented an improvement through introduction of moments of inertia obtained from the molecular spectra.

The use of quantum energies obtained directly from spectroscopic measurements was introduced by Hicks and Mitchell[10] who, at the suggestion of Tolman, dropped the assumption of rigid molecules and obtained an equation for the heat capacity of gaseous hydrogen chloride in terms of the relative energies of the individual rotation and vibration states. These were secured accurately from analysis of the fine structure of the vibration-rotation bands. This meant that the heat capacity problem became one of summing up a series of terms rather than of integrating a general expression. The former of these procedures has by far the advantage since it takes account of actually perturbing effects present in the energy terms which the more approximate equation does not give and cannot predict. Although not specifically considered in the paper of Hicks and Mitchell, their equation can be extended to cover such not uncommon influences as multiplet electronic states, missing or non-combining rotation levels, excitation of higher electronic terms, etc., by a more general choice of limits for the summations.

At that time there was still some uncertainty as to the assignment of statistical weights (also referred to as "*a priori*" probabilities) and Hicks and Mitchell, unfortunately, made an incorrect assignment which led to

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(8) (a) Dennison. *Proc. Roy. Soc.* (London), **A115**, 483 (1927): (b) Gianque and Johnston, THIS JOURNAL, **50**, 3221 (1928); (c) McClennan and MacCleod, *Nature*, 113, 152 (1929); (d) Bonhoeffer and Harteck, *Sitzb. preuss. Akad. Wiss.*, 103 (1929): *Naturwissenschaften*, **17**, 182, 321 (1929); *Z ghysik. Chem.*, **4B**, 113 (1929); (e) Eucken and Hiller, *zbid.*, **4B**, 142 (1929).

(9) Urey, THIS JOURNAL, 46, 1445 (1923).

(10) Hicks and Mitchell, *zbid.*, 48, 1520 (1926).

error in their calculations. The first correct calculation of the heat capacity of a gas other than monatomic was made by Hutchisson[11] who recalculated the heat capacity of hydrogen chloride, with correct statistical weights, from 1 to 600°K. More recently, Giauque[12] has followed this correct method in computing the heat capacity of hydrogen from near zero absolute to room temperature.

Very reliable spectroscopic data are now available for substantially all of the common diatomic gases and for several of the unstable but important diatomic molecules which appear at intermediate stages in chemical reactions. In most instances the available data for diatomic molecules are so accurate that the heat capacities, for instance, can be calculated to several thousand degrees with uncertainties of only a few hundredths of a calorie per mole per degree. We do not feel that the same claims can be made, as yet, for the calculations pertaining to any tri- or polyatomic molecule. However, for a number of the simpler tri- and polyatomic molecules data from infra-red spectra in conjunction with Raman spectra permit fairly reliable approximate values to be calculated over temperatures at which the molecules are picking up their vibrational energy and, in a more limited number of cases, their rotational energy.

The present paper is the first of a series in which we plan to compute the heat capacity curves, over comparatively wide ranges of temperature, for the common diatomic gases and for certain of the comparatively unstable diatomic molecules, such as OH. For several of the gases we will include computations of entropy[13] and of free energy.[14] In conjunction with stellar spectra, the computations at the higher temperatures should be of some assistance in the study of the physical conditions at the surfaces of certain of the stars.

The series will include more approximate calculations for certain of the tri- and polyatomic gases for which comparatively reliable data are available. We will hope to recalculate the latter when the status of the spectroscopic data warrants the more exact treatment.

The Heat **Capacity** Equation.—Three simply related quantities, independently summed, appear in the equation for heat capacity. For the sake of simplicity we will refer to these respective quantities as *A*, B and C. They are defined by the relationships:

$$A = p_i e^{-\epsilon_i/kT}; \quad B = \epsilon_i p_i e^{-\epsilon_i/kT} \quad C = \epsilon_i^2 P_i e^{-\epsilon_i/kT}$$

Here "ϵ_i" is the discrete energy, per molecule, for an individual quantum state; "P_i" the corresponding statistical weight; "*e*" the base of the natural system of logarithms and "*k*" and " T have the meanings previously assigned.

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(11) **Hutchisson,** THIS JOURNAL, *60,* 1895 (1928).

(12) **Giauque,** ibid., *52,* 4816 (1930).

(13) **Giauque and Wiebe, ibid.,** *50,* 101 (1928).

(14) **Giauque,** *ibid.,* **52,** 4808 (1930).

In terms of these symbols the heat capacity equation takes the form

$$C_V^\circ = 3/2\,R + \frac{R}{k^2T^2}\left[\frac{\Sigma C}{\Sigma A} - \left(\frac{\Sigma B}{\Sigma A}\right)^2\right] \tag{2}$$

where the sums are to be taken over *all* possible quantum states, including electronic or nuclear levels, which the molecule in question may assume. This equation gives the molar heat capacities, at constant volume, arising from all sources excepting molecular dissociation or gas imperfection.

The derivation of this important equation, in moderately simple steps, is repeated by Giauque.[14] We wish here to emphasize the essential simplicity and rigor of the underlying derivation. In using equation (2) one is essentially performing the following steps: (1) counting the numbers of molecules present in *each* discrete quantum state by application of the Maxwell–Boltzmann distribution law; (2) obtaining the *total energy content* of *each* quantum level by multiplying the number of molecules in each by their appropriate energies; (3) summing over *all* quantum levels to get the *total energy* per *mole* of gas; (4) repeating the calculation for a temperature slightly higher and (5) from this computing the increase in total molar energy per unit increase in temperature. Steps (4) and (5) are, of course, actually combined in equation (2) which is the solution of a differential equation.

The Equations for Entropy and Free Energy.—The expression for entropy takes the form

$$\begin{aligned} S^\circ - S_0^\circ = {} & 3/2\,R \ln T + R \ln V + 3/2\,R \ln M + S' \\ & + R\left[\ln \Sigma A + \frac{1}{kT}\frac{\Sigma B}{\Sigma A}\right] \end{aligned} \tag{3}$$

"S_0°" is the entropy of the gas at the absolute zero and is to be taken as identically zero if the sums in the last term are taken over *all* existent quantum states of the molecule in question.[8b,15] The first four terms to the right of the equation sign represent the entropy contribution arising from translational freedom[16] and the last bracketed term, the entropy arising from internal degrees of freedom. "V" and "M" signify molal volume and molecular weight, respectively, and "S'" is a term composed of universal constants[17] and has the value of -11.057 calories per degree per mole.

The free energy equation takes the form

$$(F^\circ - E_0^\circ)/T = 5/2\,R - S_T - R \ln \Sigma A \tag{4}$$

Here "S_T" represents the translational contribution to entropy given by the first four terms to the right of the equation sign in equation (3) and "E_0°" represents the molal internal energy of the gas at the absolute zero. It is indeterminate but the ΔE_0° appropriate to a given reaction may be

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(15) Johnston and Giauque, THIS JOURNAL, 61, 3194 (1929).

(16) Sackur, *Ann. Physik*, *36*, 958 (1911).

(17) (a) Tetrode, *Ann. Physik*, 38, 434 (1912); (b) Ehrenfest and Trkal, Proc. Akad. *Sci. Amsterdam*, 23, 162 (1920).

determined from thermochemical data or, in some cases, from spectroscopic data.

Like equation (2), equations **(3)** and (4) assume the gas to be in the hypothetical perfect state. This is indicated by the small circles above and to the right of the respective symbols. Suitable corrections for gas imperfection may be applied when desirable.

Spectroscopic Interpretation of Nitric Oxide.—The β band system of nitric oxide was discovered and photographed by E. P. Lewis.[18] The fact that the bands occur in absorption shows that the ground level is the normal state of the molecule. A careful analysis of these bands was made by Jenkins, Barton and Mulliken,[19] who photographed and analyzed some two thousand lines in thirty-six bands, under high dispersion. This work was extended recently by Schmid, Koenig and Farkas,[20] who added some thousand more lines and twenty-two more bands. The thorough work of the latter authors confirms in every detail the earlier analysis and energy assignments by Jenkins, Barton and Mulliken.

A summary of the analysis of the bands, so far as it relates to quantum assignments, has been published previously.[15] We repeat here only those facts essential to the calculations by the use of equations (2), **(3)** and (4).

The ground state of nitric oxide is a normal $^2\Pi$ state with a doublet separation of 124.4 cm.$^{-1}$ (354 calories per mole). The **A** type doubling of the rotational levels is so small that it cannot be evaluated accurately and does not affect the specific heat values, except at some small fraction of a degree absolute. Jenkins, Barton and Mulliken find that the vibrational energies, in the normal state, are quite accurately reproduced by the formulas

For the $^2\Pi_{1/2}$ **state,** $\tilde{\nu} = 1892\ 119\,v - 14.4243\,v^2 + 0.04021\,v^a - 0.001351\,v^4$ **(5a)**
For the $^2\Pi_{3/2}$ **state,** $\tilde{\nu} = 1891.976\,v - 14.4543\,v^2 + 0.04229\,v^3 - 0.001423\,v^4$ **(5b)**

where $\tilde{\nu}$ refers to the energy (in wave number units) in excess of the "zero point" energy held in the "v" $= 0$ state. The same authors find that the energies of the various rotation states for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ forms of nitric oxide are satisfactorily reproduced by the formula

$$F(J) = \text{Const.} + A(J + 1/2) + B(J + 1/2)^2 + C(J + 1/2)^3 + D(J + 1/2)^4 \qquad (6)$$

where $F(J)$ is the energy, in cm.$^{-1}$, of the rotational level characterized by a particular value of the quantum number J; the constant term represents vibrational and electronic energy; and A, B, C and D are constants whose numerical values are given in Table I.

The arrangement and spacings of the energy levels in nitric oxide, calculated from equations 5 and 6, is shown diagrammatically in Fig. 1.[21] The separations of rotational levels in (b) and of the normal doublet levels in (c) are greatly exaggerated.

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(18) **(a) Lewis, *Phys. Rev.*, [1] *18*, 125 (1904): (b) *Astrophys. J.*, *20*, 49 (1904).**

(19) **Jenkins, Barton and Mulliken, *Phys. Rev.*, 30, 150 (1927).**

(20) **Schmid, Koenig and Farkas, Z. *Physik*, 64, *84* (1930).**

(21) **With slight modification. this figure is after Mulliken, *Chem. Rev.*, 6, 524 (1929).**

TABLE I

Electronic state	A	B	C X 10^3	D X 10^5
$^2\Pi_{1/2}$	0.0071	$(1.6754 - 0.01783v)$	0.106	−0.506
	± .0081	±0.0011	± .064	± .137
$^2\Pi_{3/2}$	.0070	(1.7239 − 0.018660)	.010	− .871
	± .0121	±0.0015	± .069	± .135

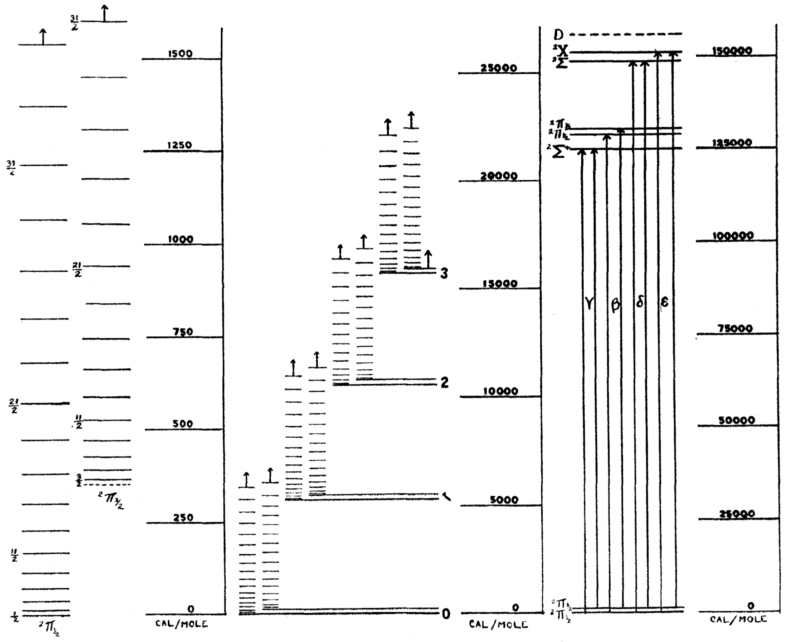
Statistical weights appropriate to the various energy states are given by the expression

$$p_i = (2J + 1)(2i_1 + 1)(2i_2 + 1) \tag{7}$$

where J is the rotational quantum number associated with the state in question and the i's represent nuclear spins. For nitric oxide, with a nuclear spin of one for nitrogen and zero for oxygen this equation reduces to

$$p_i = 3(2J + 1) \tag{7a}$$

The earlier uncertainty in respect to statistical weights has been entirely removed by the developments of the wave mechanics and the above relationship is now definitely established. The mystery formerly attached to the significance of this important quantity has also been removed. The solution of the wave equation leads to the result that for each discrete value of J associated with a particular electronic state there exist (2J + 1)



(a) Rotation levels. (b) Vibration–rotation levels. (c) Electronic levels and transitions.

Fig. 1.—Energy level diagram of NO.

$(2i_1 + 1)(2i_2 + 1)$ "eigen values" which satisfy the equation. These can be interpreted, physically, as $(2J + 1)(2i_1 + 1)(2i_2 + 1)$ different states, nearly alike in energy and all having the same electronic, vibrational and rotational quantum numbers. While the physical meaning here ascribed to statistical weights is non-essential to the immediate solutions, which depend simply on correct numerical values of p_i, this interpretation is essential to a clear conception of entropy in gases.[14]

The Heat Capacities.—Molar heat capacities of nitric oxide from 0.5 to 5000°K. were computed by the use of equation (2) and are recorded in Table II. This table is in terms of the 15° calorie and applies to nitric oxide in the hypothetical ideal gaseous condition. The tabulations represent heat capacities at constant pressure and were obtained from C_v by the addition of R calories.

TABLE II

HEAT CAPACITY OF NITRIC OXIDE IN THE HYPOTHETICAL IDEAL GASEOUS STATE

T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°
0.5	4.967	10.0	6.945	250	7.192	1250	8.389
0.6	4.970	20.0	6.973	298.1	7.144	1375	8.482
0.8	5.006	30.0	7.115	350	7.140	1500	8.561
1.0	5.120	40.0	7.363	400	7.168	1750	8.686
1.5	5.696	50.0	7.590	500	7.294	2000	8.774
2.0	6.267	62.5	7.755	600	7.476	2500	8.896
2.5	6.595	75.0	7.806	700	7.663	3000	8.982
3.0	6.758	100	7.733	800	7.840	4000	9.108
3.5	6.841	125	7.592	900	7.996	5000	9.209
4.0	6.886	150	7.468	1000	8.132		
5.0	6.912	200	7.292	1125	8.273		

The relative energies of the various vibrational and rotational states of the molecule were calculated from equations (5a, b) and (6), and the energy of the $^2\Pi_{3/2}$ state for which v = 0 and J = 3/2 was taken to be 129.55 cm.$^{-1}$ higher than that of the $^2\Pi_{1/2}$ state for which v = 0 and J = 1/2. This corresponds to an electronic coupling energy of 124.4 cm.$^{-1}$ computed from the band origins. Statistical weights were computed by equation (7a). All natural physical constants employed in the calculations were taken from the "International Critical Tables."[22] The molecular weight was taken to be 30.008.[23]

Approximations Used in Obtaining the Higher Vibration Sums.—It was found possible to avoid much of the labor incident to the higher vibration sums, without introducing appreciable inaccuracy, by the use of certain corrected approximations. As shown in Table I the rotational energies are influenced by the vibrational frequencies, so that the spacings between successive rotational levels are slightly less for states with high values of

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(22) "International Critical Tables," Vol. I, p. 16.

(23) "Thirty-Sixth Annual Report of the Committee on Atomic Weights," THIS JOURNAL, **52**, 857 (1930).

the vibrational quantum number than for the lower vibrational states. However, these effects are comparatively small and, as a first approximation, can be neglected. This is equivalent to making the assumption that B_{v+1} is approximately equal to B_v, or that for every rotational level in the vibration state with quantum number v there lies a corresponding rotational level in the state with quantum number (v + 1) whose energy is exactly $(\tilde{\nu}_{v+1} - \tilde{\nu}_v)$ higher than the energy in the lower vibrational level. On the basis of this assumption it can easily be shown that the sums for the (v + 1) level are related to those of the v level by the following equations, in which the symbol "ϵ_v" is used to replace the vibrational energy increment $(\tilde{\nu}_{v+1} - \nu_v)$

$$\Sigma_{v+1}A = e^{-\epsilon_v/kT}\,\Sigma_v A \tag{8a}$$

$$\Sigma_{v+1}B = e^{-\epsilon_v/kT}\,\Sigma_v B + \epsilon_v\Sigma_{v+1}A \tag{8b}$$

$$\Sigma_{v+1}C = e^{-\epsilon_v/kT}\,\Sigma_v C + \epsilon_v(2\Sigma_{v+1}B - \epsilon_v\Sigma_{v+1}A) \tag{8c}$$

TABLE III

THE VIBRATION SUMS FOR NITRIC OXIDE AT 2000°K.

v	ΣA Summed	Calcd.	% Correction	$\frac{1}{2.30259\,kT}\Sigma B$ Summed	Calcd.	% Correction	$\left(\frac{1}{2.30259\,kT}\right)^2\Sigma C$ Summed	Calcd.	% Correction
0	1582.80			720.54			631.01		
1	417.20	412.68	1.08	433.52	428.79	1.09	530.37	524.53	1.10
2	112.26	111.03	1.09	181.20	179.21	1.10	313.96	310.51	1.10
3	30.84	30.49	1.11	67.23	66.46	1.12	152.47	150.71	1.12
4	8.64	8.55	1.14	23.66	23.39	1.14	66.43	65.68	1.13
5	2.47*			8.12*			27.16*		
6	0.72*			2.75*			10.69*		
7	.22*			0.93*			4.12*		
8	.07*			.31*			1.57*		
9	.02*			.11*			0.54*		
10	.01*			.04*			.23*		
11	.00*			.01*			.08*		
12	.00*			.00*			.03*		
13	.00*			.00*			.01*		
Totals	2155 2			1438.4			1738.7		

Table III illustrates the application of these approximation equations to the computations at 2000°K. The columns headed "summed" give the values obtained by actual summing for the first five vibration states. The columns headed "calculated" give sums which were computed by equations (8a, b and c). The differences, in percentage, are listed in the columns headed "% correction." The near constancy in these corrections as a function of the vibration follows from the nearly linear dependence of the B constant (Table I) on the vibrational quantum number. The starred sums were computed by applying the appropriate percentage corrections to sums calculated by equations (8a, b, c). These correction factors were obtained by graphical extrapolations of the corrections evaluated empirically for the lower vibration states.

The percentage corrections necessary to the calculations by equations (8a, b, c) were also studied as a function of temperature. The results are shown in Table IV which compared the "summed" and "calculated" values for the v = 1 vibration level at four widely different temperatures

TABLE IV

THE VIBRATION SUMS FOR THE (v = 1) LEVEL OF NITRIC OXIDE AS A FUNCTION OF THE TEMPERATURE

	ΣA		% Correction	$\left(\frac{1}{2.30259\,kT}\right)\Sigma B$		% Correction	$\left(\frac{1}{2.30259\,kT}\right)^2\Sigma C$		% Correction
T, °K.	*Summed*	*Calcd.*		Summed	Calcd.		Summed	Calcd.	
1000	52.04	51.48	1.06	85.24	84.32	1.08	149.59	147.96	1.09
2000	417.20	412.68	1.08	433.52	428.79	1.09	530.37	524.53	1.10
3000	996.71	985.86	1.09	837.38	828.15	1.10	895.58	885.54	1.12
4000	1680.16	1661.71	1.10	1245.76	1231.83	1.12	1249.82	1235.52	1.14

It is evident that the correction factors do not greatly change as functions either of the vibration or of the temperature. Accordingly, for all of the higher temperatures the rotation levels were summed only for the (V = 0) levels of the two separate electronic states and the sums for the higher vibration levels were computed by equations (8a, b, c) in conjunction with the correction factors obtained by joint interpolation and extrapolation of the factors in Tables III and IV. At 1000, 2000, 3000 and 4000° the summed values for vibration states which appear in Tables III and IV were employed. In view of the rapid decrease of the sums as a function of the vibrational quantum number (cf. Table III) it is apparent that no appreciable error was introduced by this treatment.

Analysis and Interpretation of the Heat Capacity Curve.—The results are shown graphically in Figs. 2 and 3, in which open circles are used to plot spectroscopic values and dark circles mark the less reliable experimental values obtained by a calorimetric method,[24] and by a velocity of sound method.[25] These curves represent heat capacity in excess of that associated with translation and refer, in general, to heat capacity arising from rotation, from vibration and from electronic excitation.

Figure 2 includes the temperature interval from about 1°K. to approximately 5°K. over which gaseous nitric oxide takes up its rotational specific heat. There also appears, at a little higher temperature, an inflection which leads to a sharp maximum at about 75°K. This interesting maximum, predicted by Witmer,[26] shows clearly in Fig. 3 and results from the absorption of the coupling energy which separates the $^2\Pi$ electronic levels of the molecule. This behavior, which relates to a component of the specific heat never considered in the Equipartition treatment, is typical of gases which, like nitric oxide, possess a multiple normal electronic state. The temperature at which the maximum occurs and the extent of the interval over which the effect persists depends principally on the spacing of

(24) Heuse, Ann. *Physik*, **59**, 86 (1919).

(25) Partington and Shilling, *Phil.* Mag., **45**, 416 (1923).

(26) Witmer, *Phys. Rev.*, **29**, 918 (1927).

the component levels. Figure **3** also shows the vibrational contribution to the heat capacity curve, which becomes effective at about 300°K.

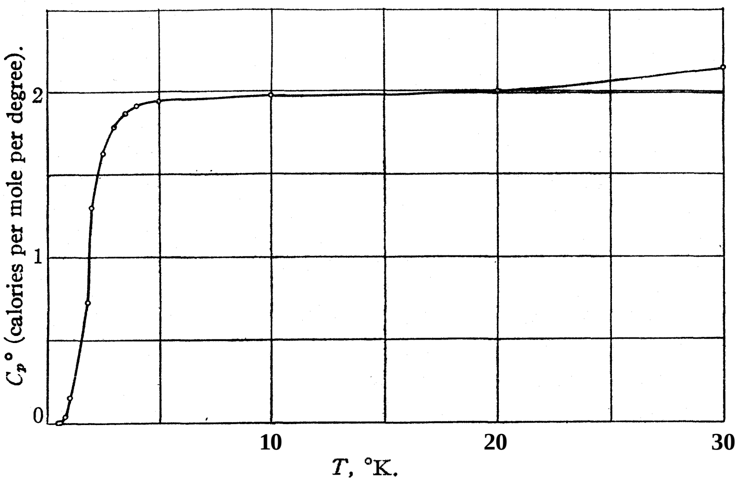

Fig. 2.—Heat capacity of gaseous nitric oxide (in excess of that due to translation).

In order to analyze in more detail the separate behavior of these several components of the total specific heat we have computed heat capacities with

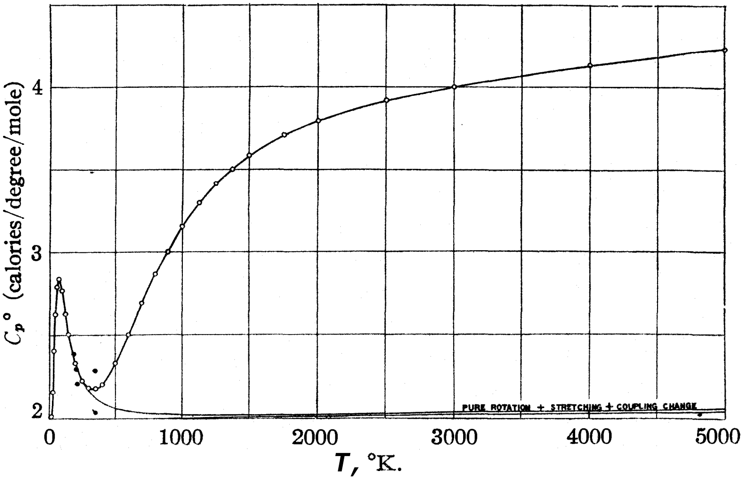

Fig. 3.—Heat capacity of gaseous nitric oxide (in excess of that due to translation): O, spectroscopic; ●, calorimetric (Heuse); $\overset{|}{\bullet}$, velocity of sound (Partington and Shilling).

certain groups of levels purposely omitted from the sums. By summing only the rotational series of the $(v = 0)$ vibration state of the $^2\Pi_{1/2}$ molecules we obtained a hypothetical pure rotation curve from which are excluded effects due to absorption of energy by either vibration or electronic excitation. This curve, which is identical with the total curve to about 15°K. and is within 0.01 calorie of rotational equipartition at 20°K., rises very gradually to a value which exceeds R by 0.05 calorie at 5000°K. This small added specific heat represents energy absorbed by centrifugal stretching at high speeds of molecular rotation. Although small in the case of nitric oxide, it typifies an effect present in all gases to a greater or less degree. Kemble and Van Vleck[27] have shown that, in hydrogen at 1350°K., the specific heat due to molecular stretching exceeds that arising from vibration. Another curve was computed by summing only the ($v = 0$) rotation series of both electronic states. This, as well as the pure rotation curve, is shown at the bottom of Fig. **3.** The differences between these curves represent specific heat arising from energy absorbed by molecules which pass from the $^2\Pi_{1/2}$ to the $^2\Pi_{3/2}$ levels while the differences between the total curve and the (Rotation + Stretching + Coupling) curve represent vibrational specific heat. At 5000°K. this equals 2.18 calories, which exceeds vibrational equipartition by 0.19 calorie, and is still rising. This results from the anharmonic character of the molecular vibration and is typical of all actual molecules. Anharmonic oscillation of a vibrator, like stretching of a rotator, adds potential energy with a consequent gain in the capacity to absorb heat. This influence has been considered previously in connection with the vibrational heat capacity of solids.[28]

A simple physical explanation of the heat capacity curve of nitric oxide can be given in terms of quantum theory by reference to the energy level diagrams of Fig. 1. At the absolute zero all of the molecules exist, under equilibrium conditions, in their state of lowest energy. This is the $^2\Pi_{1/2}$ level with $v = 0$ and $J = 1/2$ and is shown as the bottom level in the diagrams of Fig. 1 (a and b). Although the molecules perform internal oscillations due to retention of "zero point" vibrational energy, they are at rest with respect to translational motion. The immediate effect of a small increase in temperature is the appearance of kinetic energy associated with translational motion. This, in all probability, is not attained fully excited but rises rapidly to the equipartition value of 3/2 RT per mole at some small, undetermined fraction of a degree absolute. The gas thus acquires a molar translational specific heat, C_v, of 2.98 calories per degree, which corresponds to that of a monatomic gas and is represented by the base line of Fig. 2. At about 1°K. appreciable numbers of molecules begin to rise from the ($J = 1/2$) level to higher rotational levels in the same series, with consequent absorption of rotational energy. At 1°K. about 0.1 of 1% of all the molecules are in rotational levels above that for which $J = 1/2$. At 5°K. approximately 20% have reached the ($J = 3/2$) level, nearly 2% are

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(27) **Kemble and Van Vleck, *Phys. Rev.*, 21, 653 (1923).**

(28) **Rodebush, Taylor's "Treatise on Physical Chemistry," 2d ed , 1931, p. 1405.**

in the (J = 5/2) level and smaller numbers have attained higher rotational states. This redistribution toward rotational levels of higher energy continues above 5°K. with a nearly uniform rate of energy absorption.

Table V shows the temperature distribution of molecules between the levels associated with the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ isomeric forms. At 20°K. less than 1 molecule in 25,000 possesses sufficient energy to attain the lowest $^2\pi_{3/2}$ level. The absorption of the 124 cm.$^{-1}$ (353 calories per mole) coupling energy which accompanies the redistribution produces the electronic component of the specific heat.

TABLE V

PERCENTAGES OF MOLECULES IN THE $^2\Pi_{1/2}$ ELECTRONIC STATE

T, °K.	%	T, °K.	%	T, °K.	%	T, °K.	%
30	0.22	100	13.49	298.1	34.50	1000	44.81
40	0.99	126	18.53	350	36.60	2000	47.15
50	2.44	150	22.31	400	38.12	3000	48.0
62.5	4.88	200	28.04	500	40.31	4000	48.4
75	7.82	250	31.88	700	42.86	5000	48.6

The position of the maximum corresponds to the temperature at which molecules are undergoing this electronic change at the greatest *rate.*

Table VI shows the distribution of molecules among the five lowest vibration states, as a function of the temperature. The $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels are combined in this tabulation,

TABLE VI

PERCENTAGE DISTRIBUTIONS AMONG VIBRATIONAL LEVELS

	298.1	350	400	600	600	700	800	900	1000
0	99.99	99.95	99.88	99.53	98.86	97.83	96.47	94.88	93.11
1	0.01	0.05	0.12	0.47	1.13	2.12	3.39	4.84	6.40
2	0.00	0.00	0.00	0.00	0.01	0.05	0.13	0.26	0.46
3	.00	.00	.00	.00	.00	.00	.01	.02	.03
4	.00	.00	.00	.00	.00	.00	.00	.00	.00
Higher	.00	.00	.00	.00	.00	.00	.00	.00	.00
V	1125	1250	1500	1750	2000	2500	3000	4000	5000
0	90.70	88.19	83.07	78.09	73.44	65.20	58.32	47.77	40.20
1	8.40	10.37	13.98	16.99	19.36	22.48	24.06	24.66	23.73
2	0.81	1.26	2.42	3.78	5.21	7.88	10.07	12.86	14.13
3	.08	0.16	0.43	0.87	1.43	2.81	4.27	6.77	8.48
4	.01	.02	.08	.21	0.40	1.02	1.83	3.61	5.13
Higher	.00	.00	.02	.06	.16	0.61	1.45	4.33	8.33

At room temperature only 1 molecule in 10,000 has gained vibrational energy in excess of that which it possessed at the absolute zero.(29) Above

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(29) Table XII of Ref. 14 is in error in so far as it applies to vibration states higher in energy than those for which $v = 0$ (there identified by "n" = 1/2) through an inadvertent error in the value used for the vibrational energy. This necessitates a correction in $S_{298.1}$, which should read 50.35 E. U., as given in this paper. The error to which we refer in no wise affects the comparison of calorimetric and spectroscopic entropies at 121.36°K., or the important conclusions with respect to the use of the Third Law of Thermodynamics. A typographical error also occurred on p. 3211 where brackets were omitted from the equation for S_{E+V+R}.

room temperature appreciable numbers of molecules acquire frequencies corresponding to higher overtones, with attendant increase in the rate of energy absorption.

The Entropy of Nitric Oxide.—Table VII gives the entropy of nitric oxide calculated by equation (3) for temperatures ranging from 1 to 5000°K. These values refer to the hypothetical ideal gaseous state at a pressure of 1 atmosphere and are expressed in calories per mole per degree.

TABLE VII

ENTROPY OF NITRIC OXIDE IN THE IDEAL GASEOUS STATE AT 1 ATMOSPHERE PRESSURE

(Nuclear Spin Entropy Not Included)

T, °K.	$S°$	T, °K.	$S°$	T, °K.	$S°$	T, °K.	$S°$
1	10.617	75	40.028	400	52.449	1250	61.234
5	20.672	100	42.267	500	54.062	1500	62.780
10	25.477	125	43.978	600	55.408	1750	64.111
20	30.295	150	45.350	700	56.573	2000	65.275
30	33.145	200	47.473	800	57.607	2500	67.248
40	35.227	250	49.088	900	58.474	3000	68.877
50	36.896	298.1	50.350	1000	59.392	4000	71.481
62.5	38.609	350	51.494	1125	60.356	5000	73.526

In obtaining these values we have subtracted the multiplicity of 3 arising from the one unit of nuclear spin associated with the nitrogen nucleus. Hence, in order to obtain the total absolute entropy of nitric oxide the values in the above table must all be increased by $R \ln 3 (= 2.18)$ entropy units. However, it is probable that for nitrogen, as for iodine,[30] this entropy is carried by the nitrogen atom into its various chemical combinations and so cancels out[31] when one computes the entropy *change* which occurs in a reaction. For that reason we do not include it in the table, which gives the values that should be employed in thermodynamic calculations involving nitric oxide gas. It is, of course, understood that these entropies are to be combined with entropies which likewise omit the nuclear spin entropy arising from the presence of nitrogen atoms. In all probability the nuclear spin entropy of nitrogen will be absent from the entropies obtained calorimetrically for nitrogen compounds.

The usual method of getting the entropy of a chemical substance is by graphical or analytical integration of $\int_{T'}^{T} C_p \, d \ln T$, in which the lower limit of integration represents a temperature so low that the heat capacity approaches zero asymptotically and so can be extrapolated to a negligible value with little error in the resulting area under the curve. Giauque and Johnston[5b] and Johnston and Giauque[15] have pointed out that reliable calorimetric information, alone, is sometimes insufficient to give the correct value of the entropy for use in thermodynamic calculations. An interesting illustration of this, which shows clearly the reason for the point in

(30) Giauque, THIS JOURNAL, 53, 507 (1931).

(31) Gibson and Heitler, *Z. Physik*, 49, 465 (1928).

question, is provided in the computations for gaseous nitric oxide. We believe that the heat capacities which we have calculated represent the values which would be approached by accurate calorimetric determinations corrected for gaseous imperfection, and that if 100% accurate calorimetric measurements could be made on the hypothetical perfect gas down to, say, 1°K., the curves which we have shown would be reproduced. Such a curve could easily be extrapolated to a negligibly low value below 1°K. Yet if data so obtained were plotted against the natural logarithm of the temperature, the correct entropy values of Table VII would not be obtained. We show this in Table VIII which was obtained by graphical integration of the values recorded in Table II. It will be observed that the graphical values lie under the exact equation (3) values by R ln 4 (=2.76) entropy units.

TABLE VIII

"INCORRECT" ENTROPY OBTAINED GRAPHICALLY FROM THE HEAT CAPACITY CURVE

T, °K.	"$S°$"	T, °K.	"$S°$"	T, °K.	"$S°$"	T, °K.	"$S°$"
1	7.87	20	27.54	298.1	47.58	2000	62.52
5	17.91	50	34.14	500	51.30	3000	66.12
10	22.73	100	39.51	1000	56.62		

The explanation, in this case, is quite simple. Up to the present we have referred to the lowest level of nitric oxide as the ($J = 1/2$) level of the ($v = 0$) vibration state of the $^2\Pi_{1/2}$ molecule, and have represented this level by a single horizontal line in Fig. 1 (a and b). In reality this level itself consists of four very close component levels (we still exclude the influence of nuclear spin) among which the molecules are evenly divided at 1°K., and even down to somewhat lower temperature. This multiplicity is in consequence of two factors: (1) the double statistical weight of the ($J = 1/2$) rotational level by equation (7) which means, physically, two distinct quantum states of the molecule and (2), the doubling of the electronic level. This multiplicity did not contribute to the heat capacity curve above 1°K. because its effect was spent below this temperature, in much the same way that the $^2\Pi$ coupling energy had practically spent its effect below 500°K. At some temperature below 1°K., probably at a few hundredths of a degree absolute, there should exist a very narrow, but possibly quite high, specific heat maximum which represents the equilibrium transformation between the two Λ types of the molecules. The area under the C_v vs. T curve, through this maximum, represents the small energy of transformation of half a mole of the lower energy modification into the higher energy form. In nitric oxide, this Λ coupling energy is too small for evaluation although sufficiently large to permit spectroscopic resolution of the doublets which comprise the higher rotation lines. The double weight of the ($J = 1/2$) level must also lead to a narrow maximum at a still lower temperature, due to the slight energy difference which must arise between the two rotational forms as a result of the perturbing influence of weak fields, such as the magnetic field of the earth. It is omission of these effects, necessary to the complete heat capacity curve, that led to the incorrect values in Table VIII. The proper correction may readily be applied when there is recognition, as in this case, of the existence of the equimolar, four component mixture whose entropy of mixing is $R \ln 4$ as given by the Second Law of Thermodynamics.

Free Energy Values and the Degree of Dissociation.—In Table IX we give values of $-(F^\circ - E_0^\circ)/T$ for gaseous nitric oxide at a pressure of one atmosphere. Underscored values were calculated by equation (4). The remainder were interpolated by a graphical method.

TABLE IX

"FREE ENERGY" OF GASEOUS NITRIC OXIDE

T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
75	32.747	1100	52.598	2900	60.285
100	34.862	1125	52.766	3000	60.567
125	36.520	1150	52.932	3100	60.841
150	37.881	1200	53.259	3200	61.107
200	40.029	1250	53.570	3300	61.365
250	41.685	1300	53.871	3400	61.616
298.1	42.985	1375	54.303	3500	61.860
300	43.033	1400	54.442	3600	62.097
350	44.163	1500	54.979	3700	62.328
400	45.141	1600	55.483	3800	62.553
450	45.999	1700	55.960	3900	62.772
500	46.769	1750	56.191	4000	62.986
550	47.465	1800	56.413	4100	63.196
600	48.100	1900	56.844	4200	63.401
650	48.687	2000	57.255	4300	63.601
700	49.228	2100	57.648	4400	63.796
750	49.738	2200	58.024	4500	63.987
800	50.214	2300	58 384	4600	64.174
850	50.663	2400	58.730	4700	64.357
900	51.088	2500	59.063	4800	64.537
950	51.491	2600	59.385	4900	64.714
1000	51.878	2700	59.695	5000	64.888
1050	52.244	2800	59.995		

This table will find eventual application in a large number of reactions involving gaseous nitric oxide. Immediate application can be made to the equilibria involved in the decomposition of the gas into its elements. The more important of these equilibria is that between the gas and molecular nitrogen and molecular oxygen, which forms the basis of the Birkeland–Eyde process for the fixation of atmospheric nitrogen. This equilibrium will be discussed by Giauque and Clayton in a paper soon to appear in THIS JOURNAL. A less important, but nevertheless interesting, equilibrium is that between molecular nitric oxide and nitrogen and oxygen atoms. Consider the reaction NO = N + O.

For this reaction

$$\frac{\Delta F^\circ}{T} = \frac{F^\circ(\mathrm{O})}{T} + \frac{F^\circ(\mathrm{N})}{T} - \frac{F^\circ(\mathrm{NO})}{T}$$

$$= \left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{O}} + \left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{N}} - \left(\frac{F - E_0^\circ}{T}\right)_{\mathrm{NO}} + \frac{\Delta E_0^\circ}{T}$$

The term in $(F^\circ - E_0^\circ)/T$ for NO, is taken from Table IX; the corresponding term for atomic oxygen is taken from the table prepared by Johnston and Walker;[32] and that for atomic nitrogen is calculated by equation (4) with ΣA put equal to

$$4 + 10e\,\frac{-54{,}640}{RT} + 6\,e\,\frac{-82{,}070}{RT}$$

The statistical weights and the energies appropriate to the latter expression are derived from consideration of the spectrum of the neutral nitrogen atom, which has been worked out by Compton and Boyce.[33] ΔE_0° is the heat of dissociation at the absolute zero and is identical with the spectroscopic "heat of dissociation" into normal atoms. This quantity is not known for nitric oxide with any high degree of accuracy. Hence we can calculate, at present, only the order of magnitude of the dissociation. Taking ΔE_0° to be 142,000 calories per mole, which Mulliken[34] estimates as correct to within 5000 to 15,000 calories, we obtain the figures in Table X.

TABLE X

APPROXIMATE VALUES OF THE DISSOCIATION OF NITRIC OXIDE INTO ATOMS AT A TOTAL PRESSURE OF 1 ATMOSPHERE

T, °K.	ΔF°	K	α
2000	88,468	2.15×10^{-10}	1.47×10^{-5}
3000	58,842	5.16×10^{-5}	7.18×10^{-3}
4000	29,668	2.39×10^{-2}	0.153
5000	19,820	0.136	0.346

The equilibrium constant K was obtained from the thermodynamic relationship $AF^0 = -RT \ln K$ and the degree of dissociation, α, was computed from the relationship $\alpha = \sqrt{K/(K + P)}$, with P put equal to 1. Although we must regard these figures as correct only in the order of magnitude, they serve to indicate the relatively high stability of nitric oxide with respect to dissociation into atoms. The instability which attaches to nitric oxide at moderate temperatures exists in virtue of the unusually high stability of the nitrogen molecule, favoring dissociation in that direction, and is not due to any intrinsic instability of the NO molecule.

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(32) Johnston and Walker, THIS JOURNAL, 55, 187 (1933).

(33) Compton and Boyce, *Phys. Rev.*, **33**, 145 (1929).

(34) Mulliken, *Chem. Rev.*, 9, 347 (1932).

Evaluation of the Limits of Error.—Except for small uncertainties in the physical constants employed, which influence the final figures to an almost negligible degree (this uncertainty may influence the values in Tables VII and IX by as much as 0.01 calorie; the influence on heat capacities would be only about one-tenth of this), the extent to which values in the preceding tables may be in error is determined by the accuracy of the spectroscopic data or, more properly, of the equations for the vibrational and rotational energies (Equations (5a, b), 6). Below 1000°K. substantially all of the terms needed in accurately evaluating the several sums lie within the range of energies covered by spectroscopic observations which the energy equations accurately reproduced. Even at 5000°K. the several higher vibration levels which made appreciable contributions to the sums were almost entirely represented in the observed bands. Thus only 0.07% of ΣA, 0.37% of ΣB and 1.21% of ΣC were contributed by vibration levels which represented extrapolations of energies by the accurate equations (5a, b). A considerably larger fraction of the rotational sums was contributed, at the higher temperatures, by rotational terms whose energies lay beyond the spectroscopic observations. This is illustrated in Table XI which shows: (1) the total number of rotational terms summed in the $^2\Pi_{1/2}$ ($v = 0$) vibrational level, and (2) the number of those terms, starting with the ($J = 1/2$) term, which contributed 90% of the totals to the respective sums. The actual spectroscopic data covered the first 32 rotational terms. It was thus necessary, at these higher temperatures, to employ equation (6) to compute the energies of many rotational terms which represent an extrapolation beyond those observed experimentally. However, this does not constitute a serious source of error since the equation of Jenkins, Barton and Mulliken will certainly give the first several extrapolated energies with considerable accuracy and since the higher extrapolations, which may be relatively inaccurate for purposes of spectroscopy,[35] involve terms with energies so large that the same degree of accuracy is not essential in their evaluation. Indeed, for an equation which will faithfully reproduce the first thirty-two terms in the rotational series, the increase in the error on passing from term to term in the high rotational extrapolations will probably be more than offset by the dwind-

TABLE XI

THE NUMBERS OF ROTATIONAL TERMS WHICH CONTRIBUTED APPRECIABLY TO THE ROTATIONAL SUMS OF THE $^2\pi_{1/2}$ ($v = 0$) STATE

T, °K.	Total (all sums)	Terms contributing 90% of the respective sums ΣA	ΣB	ZC
1000	81	30	40	55
2000	168	55	65	75
5000	200	70	90	115

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(35) Cf. Kemble, *Phys. Rev.*, 30, 387 (1927), for a form of rotational energy equation more appropriate to the type of electronic binding present in NO

ling importance of the successive terms. Accordingly, we believe that we can make a fair estimate of the extent to which the calculated data are in error by considering the probable errors assigned to the constants in their rotational energy equation, by Jenkins, Barton and Mulliken. These were given in Table I. In computing the error which may exist in the values in our tables we assumed the case most unfavorable to ourselves, namely, that the probable errors to the several constants in equation (6) were all present at full value and of such sign that they were all additive. This is a rather extreme assumption and the tables are probably somewhat more accurate than indicated by the errors which we compute.

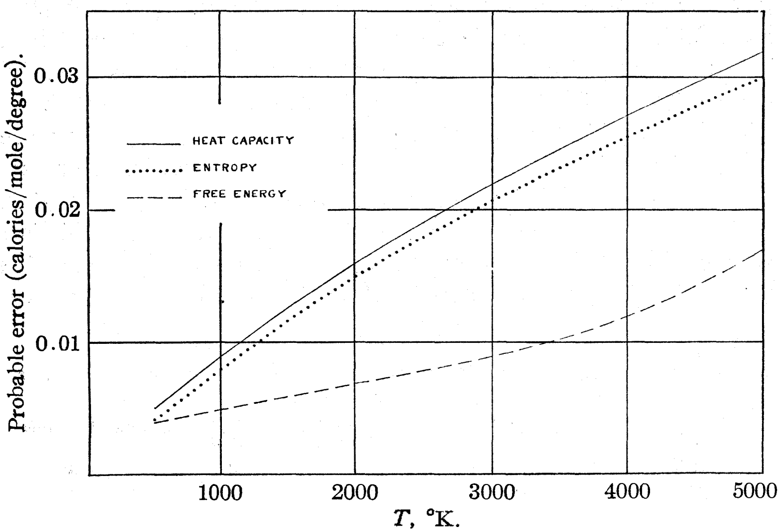

Fig. 4.—Probable errors in the spectroscopic values of C_p°, of S° and of $((F^\circ - E_0^\circ)/T)$ for nitric oxide.

In making the actual computations of the probable error we employed a method which is an extended form of that used by Hutchisson.[11] This depends on the recognition that a certain percentage error in ϵ_i is equivalent to the same percentage error (of opposite sign) in T, since T appears under ϵ_i in all of the equations which we employ in evaluating the sums. By plotting the respective sums against T, on a large-scale graph, it is thus possible to estimate the needful corrections for a small correction in ϵ_i. For hydrogen chloride at low temperatures Hutchisson needed to consider the probable error only in the B constant of the rotational energy equation and so could assume a constant percentage error to apply to all of the energy terms which make up a given sum. With nitric oxide at high temperatures the influence of the different rotational constants produced a variable effect on the energies of the various rotational terms. It was thus necessary to use a weighted average for the percentage probable error of the temperature term for the sums. We accomplished this by dividing the rotational terms into successive groups of ten; computing the average percentage error in the energies of the ten terms composing a group; and computing a weighted mean by considering separately the proportional contributions of the several decimal groups to Σ's A, B and C in turn. The heat capacity, entropy and free energy were then recalculated from these "corrected" sums and the divergences were noted. This procedure was followed for temperatures of 500, 1000, 1500, 2000, 2500, 3000, 4000 and 5000°. The results are shown graphically in Fig. 4 in which separate curves are drawn to represent the probable errors in the various tables. It is noteworthy that even at 5000°K. the probable errors in none of these quantities exceed 0.03 calorie while at 500°K. the errors do not exceed 0.005 calorie.

We wish to acknowledge a grant from the National Research Council, which has been applied to the purchase of an electric computing machine to aid in the subsequent investigations in this series.

Summary

The importance of accurate values for gaseous specific heats has been stressed and attention has been called to the present unreliability of experimental values.

Equations based on quantum theory, which permit accurate calculation of heat capacity, entropy and "free energy," have been discussed.

The heat capacity of nitric oxide in the ideal gaseous state has been calculated for the temperature range 0.5 to 5000°K. The heat capacity curve shows a sharp rise between approximately 1 and 5°K., which represents the attainment of rotational equipartition; a maximum at about 75°K., which results from excitation to the upper level of the normal $^2\Pi$ electronic state of the molecule; and a vibrational component which starts at about 300°K. and attains the equipartition value at about 3000°K. At high temperatures the rotational component of the specific heat exceeds the equipartition value, due to centrifugal stretching of the molecule, and the vibrational component exceeds R calories, due to the anharmonic character of the oscillations.

Tables are included which show the temperature distributions of nitric oxide molecules between the electronic levels of the normal doublet and between the various vibrational levels.

The entropy has been calculated and tabulated for temperatures from 1 to 5000°K. The fact that heat capacity data alone are sometimes insufficient to give the full entropy is reaffirmed.

The "free energy," as represented by the quantity $-(F^\circ - E_0^\circ)/T$ has been calculated from 75 to 5000°K. and tabulated in a fashion that permits easy interpolation.

Approximate values are given for the degree of dissociation into atoms, at one thousand degree intervals. The approximate character of the computations results from present uncertainty in the heat of dissociation. The computations show that nitric oxide is intrinsically stable with respect to dissociation into its atoms at moderate temperatures.

Certain corrected approximations which permit reliable computations of the higher vibrational sums with a considerable saving in labor are discussed.

The probable errors of the heat capacity, entropy and "free energy" calculations are determined. For each of the three quantities they amount to only about 0.03 calorie per mole per degree at 5000°K. and to less than 0.005 calorie per mole per degree at 500°K.

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Heat Capacity Curves of the Simpler Gases. II. Heat Capacity, Entropy and Free Energy of Gaseous Oxygen from Near Zero Absolute to 5000°K.[1]

BY HERRICK L. JOHNSTON AND MARGERY K. WALKER

The chemical importance of oxygen lends particular interest to the evaluation of its heat capacity, entropy and free energy. From a theoretical standpoint the heat capacity curve possesses added interest due to the multiple nature of the normal electronic level, the absence of alternate rotational states and the comparatively low energy of some of the excited electronic levels. The more than usual reliability of the spectroscopic data on molecular oxygen, both in point of interpretation and in point of accurate wave length determinations, permits the attainment of high accuracy in the calculations.

In this paper we present the results of heat capacity, entropy and free energy calculations to a maximum temperature of 5000°K. The calculations were carried out in the manner described in the previous paper.[2] The reader is referred to that paper for the meanings of symbols which we here employ without redefinition.

Spectroscopic Interpretation of Molecular Oxygen.—Two band systems are prominent in the spectrum of molecular oxygen. These are the Schumann–Runge system, which occurs in the ultraviolet and has been extensively photographed both in emission[3] and in absorption,[4] and the

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(1) Presented March 31, 1931, as part of the symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

(2) Johnston and Chapman, THIS JOURNAL, 55, 153 (1933).

(3) Runge, *Physica*, 1, 254 (1921).

(4) (a) Schumann, "Smithsonian Contributions to Knowledge," 29, No. 1413 (1903); (b) L. and

"atmospheric absorption" system,[5] so called because of its prominence among the Fraunhofer lines which have been identified as arising from absorption of solar radiation by the earth's atmosphere. This system lies in the near infra-red. The fact that both systems make their appearance by absorption in cold gas shows that their common ground state is the normal level of the molecule.

These experimental data were successfully analyzed and interpreted through the efforts of Ossenbrüggen[6] and of Mulliken.[7] The structure assigned to the oxygen molecule by Mulliken accorded also with the magnetic behavior of molecular oxygen[8] and was subsequently confirmed by the identification and analysis of nearly a hundred faint lines which had their origin in oxygen molecules containing the isotopic atoms O^{18} and O^{17}.[9]

A summary of the analyses of the atmospheric bands, in so far as it relates to quantum assignments, has been published previously.[10] We repeat here only those facts essential to the calculations in the present paper.

The ground state of the oxygen molecule is a $^3\Sigma$ state whose three components are termed, by Mulliken, the F_1, F_2 and F_3 coupling states, respectively. The coupling energy of the F_2 form exceeds that of the other components by about 2 cm.$^{-1}$ (6 calories per mole). One equation serves equally well to represent the vibrational levels of all three forms. In the calculations included in the present paper we have adopted the vibrational formula

$$\tilde{\nu} = 1565.37v - 11.37v^2 \qquad (1)^{11}$$

which was derived by Birge and Sponer[12] from a careful analysis of the extensive data on the Schumann–Runge bands.[3,4a,b,c,d,e] $\tilde{\nu}$ here refers to the vibrational energy (in wave number units) in excess of the "zero point" vibrational energy retained by the molecules in their lowest level, ($v = 0$).

Equations for the rotational energies of molecular oxygen have been given by Dieke and Babcock,[5e] by Ossenbrüggen[6] and by Mecke and Wurms.[13] Expressed in the modern notation, these all take the form

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E. Bloch, Compt. rend., **158**, 1161 (1914); (c) Duclaux and Jeantet, ibid., **173**, 581 (1921); (d) Leifson, Astrophys. *J.*, **63**, 73 (1926); (e) Fuchtbauer and Holm, Physik. Z., **26**, 345 (1925); (f) Malan, *Compt. rend.*, **192**, 1720 (1931).

(5) (a) Lester, Astrophys. *J.*, **20**, 81 (1904); (b) Fortrat, Ann. *J.* Phys., **3**, 384 (1915); (c) Meggers, Pub. Allegheny Observatory, 6, No. 3 (1919); (d) Babcock, *Astrophys.* J, **65**, 140 (1927); (e) Dieke and Babcock, Proc. *Nat.* Acad. *Sci.*, **13**, 670 (1927); (f) Badger and Mecke, *Z.* Physik. **60**, 59 (1930); (g) Mecke and Baümann, ibid., **73**, 139 (1931).

(6) Ossenbrüggen, ibid., **49**, 167 (1928).

(7) Mulliken, Phys. Rev., **32**, 213, 880 (1928).

(8) Van Vleck, ibid., **31**, 608 (1928).

(9) Giauque and Johnston, THIS JOURNAL, **51**, 1436, 3528 (1929).

(10) Giauque and Johnston, ibid., **51**, 2300 (1929).

(11) Recent very accurate measurements of the (1,1) absorption band of atmospheric oxygen [Babcock, Phys. *Rev.*, **35**, 125 (1930) and also Ref. 5g] give 1556.31 cm.$^{-1}$ and 1556.41 cm.$^{-1}$, respectively, for the relative energy of the $v = 1$ vibrational level. These values are to be preferred to the value 1554.0 cm.$^{-1}$ obtained by the use of equation (1) but recalculation of certain of our heat capacity, entropy and free energy values on the basis of the more accurate energy produced no change in the third decimal, even for quite high temperatures, at which the vibrational levels become relatively more effective.

(12) Birge and Sponer, Phys. Rev., **28**, 259 (1926).

(13) Mecke and Wurms, *Z.* Physik, **61**, 37 (1930).

$$F(K) = B[K(K+1)] - D[K^2(K+1)^2] \qquad (2)$$

where $F(K)$ is the energy, in cm.$^{-1}$, of the rotational level characterized by a particular value of the rotational quantum number K, and B and D are numerical constants. Values given for the numerical constants appropriate to the ($v = 0$) vibrational level of normal ▪▪ oxygen are summarized in Table I.

TABLE I

ROTATIONAL ENERGY CONSTANTS OF THE (v = 0) VIBRATIONAL LEVEL OF THE NORMAL $^3\Sigma$ STATE OF MOLECULAR OXYGEN

Authors	B	D
Dieke and Babcock	1.438	6.31×10^{-6}
Ossenbriiggen	1.4380	4.9×10^{-6}
Mecke and Wurms	1.4375	4.77×10^{-6}

Giauque and Johnston[8] found that the "D" constant of Dieke and Babcock was in error since, for high rotational quantum numbers, the equation given by the latter authors failed to reproduce, with sufficient accuracy, the data from which it was derived. A better value of this constant can be obtained by making use of a theoretical relationship which relates it to the value of "B" and to the vibrational constants.[14] By this method we obtain $D = 4.86 \times 10^{-6}$. With this correction the equation of Dieke and Babcock becomes substantially identical with that of Ossenbruggen, and of Mecke and Wurms, and is in good agreement with the experimental values for the rotational energies. In the calculations included in the present paper we have employed the rotational energy formula

$$F(K) = (1.438 - 0.01596v)\,K(K+1) - 0.00000486K^2(K+1)^2 \qquad (2a)$$

which includes a correction term ($0.01596v$,), for the variation of "B" with the vibrational quantum number v, as found by Mecke and Baumann.[5g] Since only the alternate rotational levels are present in the oxygen molecule,[5e,f,g,6,7,9,15] only odd values of K are to be used with equation (2a).

Equation (2a) yields, accurately, the rotational energies of those molecules which possess the F_2 form of electronic coupling in the normal $^3\Sigma$ state. The energy of an isomeric F_1 or F_3 molecule is approximately 2 cm.$^{-1}$ less than that of an F_2 molecule with the same rotational quantum number K. This difference in electronic coupling energy between the isomeric forms of the multiplet normal level is responsible for the appearance of doublets in the spectrum of molecular oxygen. Measurement of the widths of these doublets provides a means of obtaining the energy levels of the F_1 and F_3 molecular species.

Making use of the data of Dieke and Babcock,[5e] supplemented by the more recent data of Babcock,[9,16] we have computed the energies of mole-

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(14) Cf. Birge, *Bull. Nat. Rec. Council*, **11**, 172 (1926).

(15) Mecke, *Physik. Z.*, **26**, 233 (1925)

(16) Babcock, *Proc. Nat. Acad. Sci.*, 16, 471 (1929).

cules in the F_1 and F_3 states relative to molecules in the F_2 state for rotational quantum numbers to "K" = 25. The results are represented graphically in Fig. 1, which includes data from the isotopic O^{16}–O^{18} molecule as well as from the ordinary O^{16}–O^{16} molecule. This use is permitted since the electronic isotope effect is small and is quite negligible for the 2 cm.$^{-1}$ difference in electronic energy of coupling involved in these calculations. The inclusion of data pertaining to the isotopic molecule yields coupling energies appropriate to even as well as to odd rotational levels since alternate levels are missing only for the symmetrical O^{16}–O^{16} molecule. In obtaining Fig. 1 we have used all the spectrum lines which yielded the appropriate combinations, without regard to their relative reliability. In obtaining Fig. 2 we have excluded all calculations which involved a line marked in the tables of Dieke and Babcock, or of Babcock, as "double"

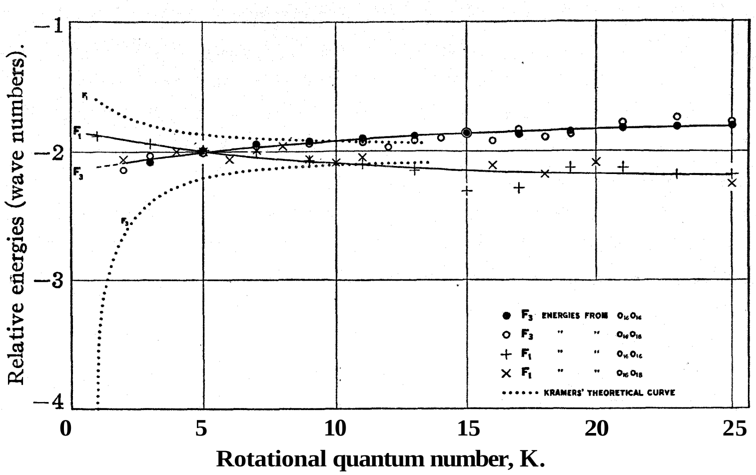

Fig. 1.—Energies of the F_1 and F_3 rotational levels of normal oxygen related to the F_2 levels.

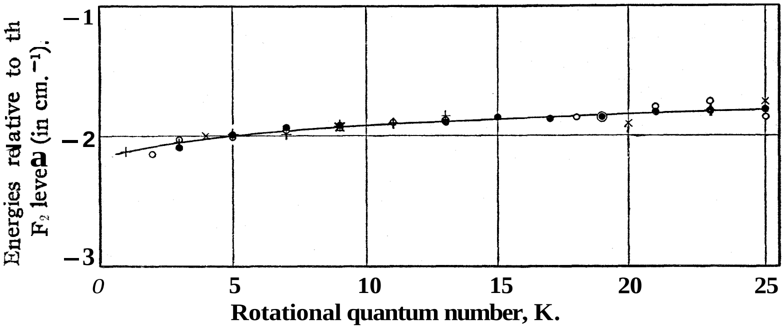

Fig. 2.—Interpolation curve for obtaining smoothed values of the coupling energies.

or as "used in more than one series" resulting from coincidence or near coincidence of lines with others of the oxygen spectrum or with lines of the solar spectrum. We have also taken advantage of the relationship, first noted by Mulliken,[7] that the experimental curves for the energies of the F_1 and F_3 levels, relative to the F_2, are symmetrical around 2 cm.$^{-1}$. We have rotated the F_1 energy values around this coordinate as an axis and so obtained a common curve utilizing the data from both the P doublets and the R doublets of the spectrum. The curves through the experimental data in Fig. 1 were constructed by symmetrical transposition of the curve obtained in Fig. 2.

The non-appearance in the spectrum of the line corresponding to the $(J = 0) \longrightarrow (J = 0)$ transition precludes the direct experimental evaluation of the relative energy of the F_3 level with $K = 1$. For the present calculations we have taken the energy of this level to be 2.13 cm.$^{-1}$ beneath that of the corresponding F_2 level. We obtained this value by direct extrapolation of the F_3 curve of Fig. 1. However, we wish to call attention to the possibility of an error introduced by this extrapolation. Kramers[17] has derived a wave mechanical formula which gives the separations to be expected among these multiplet levels, as a function of the rotational quantum number. His equation does not give very good quantitative agreement with the experimental values, as is apparent in Fig. 1, which includes curves derived from Kramers' equation. This lack of agreement (in a quantitative sense) is attributable in part to failure to carry the laborious mathematical analyses beyond the second approximation and, in part, to the introduction of certain simplifying assumptions regarding the nature of the molecule which fail to make allowance for actual perturbing influences which do exist. Professor Mulliken[18] has called our attention to the fact that probably Kramers' formula will apply to the one level we are here considering. This results from the fact that the perturbations referred to above are produced by an interaction between levels with the same J value. The level in question is unique in standing alone in its J value $(J = 0)$ and so escapes the perturbation. Should this analysis be correct we should take the energy of this level as 4.0, rather than as 2.13 cm.$^{-1}$ below the corresponding F_2 level. However, there is still some uncertainty on this one point of analysis and in the absence of either a direct experimental value or of an unquestioned theoretical derivation, we choose to employ the value extrapolated from adjacent rotational levels, and yielded by the symmetry of the F_1 and F_3 curves. An error of 2 cm.$^{-1}$, which is the uncertainty involved in the relative energy of this one level, produces an altogether negligible effect on the calculated heat capacities, entropies and free energies above 10°K. But below 10°K. a 2 cm.$^{-1}$ error in this

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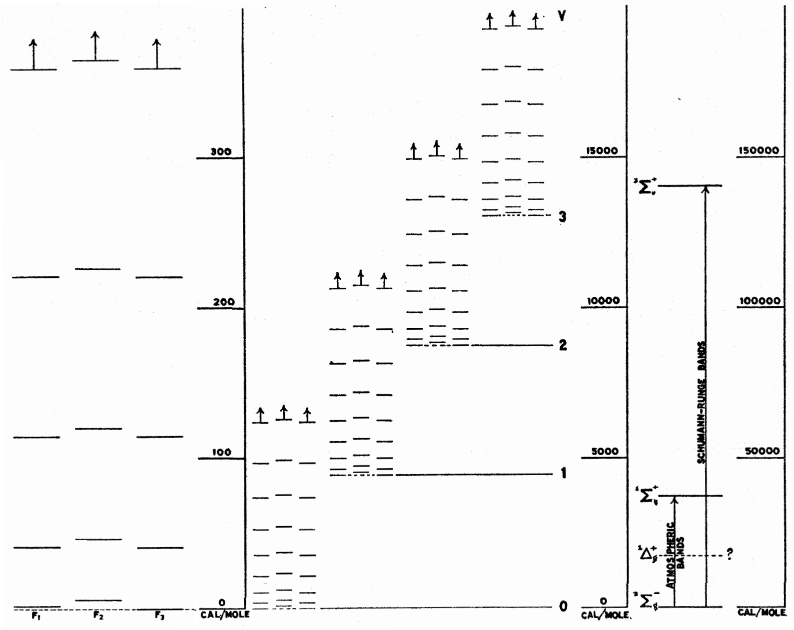
(17) Kramers, *Z Physik*, **53**, 422 (1929).

(18) Mulliken, private communication.

one level would appreciably influence the quantitative relationships—although not the qualitative character—of the interesting inflections in the heat capacity curve, which is reproduced in Fig. 4.

The arrangement and spacings of the energy levels in oxygen are shown diagrammatically in Fig. 3. The separations of rotational levels in (b) are greatly exaggerated.



(a) Rotation levels. (b) Vibration–rotation levels. (c) Electronic levels and transitions.

Fig. 3.—Energy level diagram of O_2.

Statistical weights appropriate to the various energy states are given by the expression

$$p_i = (2J + 1) \tag{3}$$

where $J = (K + 1)$, (K) and $(K - 1)$ for the F_1, F_2 and F_3 forms, respectively. The terms in i drop out[19] since oxygen is without nuclear spin.

The Heat Capacities.—Molar heat capacities of gaseous oxygen from 0.020 to 5000°K. have been calculated with the aid of equation (2) from the previous paper.[2] Table II summarizes the results of the calculations for the interesting temperature interval below 10°K. The tabulations refer to the hypothetical ideal gaseous state, at constant volume, and do not include the 2.980 calories per mole per degree associated with the translational motion of the molecules. The heat capacity curve, shown in Fig. 4, was constructed from the values included in Table II. The two maxima

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(19) Cf. Equation 7 of Ref. 2.

TABLE II

ROTATIONAL AND ELECTRONIC HEAT CAPACITY OF GASEOUS OXYGEN BETWEEN 0.02 AND 10°K.

T, °K.	C_v°	T, °K.	C_v°	T, °K.	C_v°
0.020	0.000	0.115	2.856	1.50	0.479
.025	.001	.120	2.866	1.75	.436
.030	.006	.125	2.850	2.00	.402
.040	.078	.150	2.545	2.50	.385
.050	.319	.175	2.105	3.00	.465
.065	1.026	.200	1.695	4.00	.856
.075	1.595	.250	1.100	5.00	1.311
.080	1.866	.350	0.522	6.00	1.647
.085	2.123	.500	.352	7.00	1.844
.090	2.327	.750	.426	8.00	1.942
.095	2.507	1.000	.501	9.00	1.984
.100	2.647	1.250	.510	10 00	1.999

which occur below 2°K.—one extending to a height of nearly three calories—are electronic heat capacity curves and result from the absorption of energy by molecules which undergo transition from the F_3 to the F_1 and F_2 forms of coupling. They are analogous to the prominent maximum which occurs in the specific heat curve of nitric oxide at about 75°K.[2] Their occurrence at a much lower temperature, in oxygen, is due to the much smaller coupling energy in molecular oxygen as compared with nitric oxide. The steep rise between 2 and 10°K. represents the growth of the rotational specific heat.

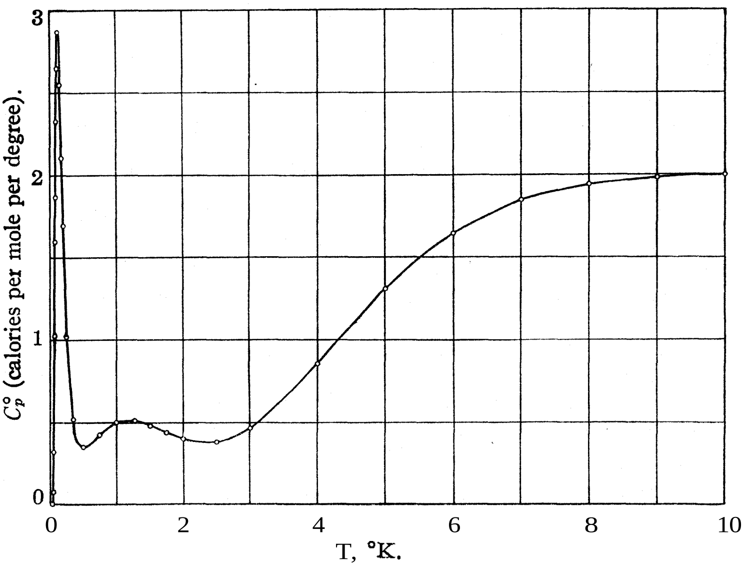

Fig. 4.—Heat capacity of gaseous oxygen (in excess of that due to translation).

The heat capacities at higher temperatures are tabulated in Table III and the results are shown graphically in Fig. 5.

TABLE III

HEAT CAPACITY OF GASEOUS OXYGEN IN THE HYPOTHETICAL IDEAL STATE (INCLUDING TRANSLATION)

T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°
11	6.967	25	6.950	500	7.434	1500	8.702
12	6.969	50	6.962	600	7.675	1750	8.802
13	6 965	75	6.962	700	7 890	2000	8.880
14	6.962	90.13	6.962	800	8.069	2500	9.001
15	6.959	200	6.961	900	8.216	3000	9.108
16	6.956	298 1	7.018	1000	8.339	4000	9.329
20	6.950	400	7.197	1250	8.558	5000	9.554

The results here refer to heat capacities at constant pressure and include the translational contribution. Open circles are employed, in Fig. 5, to represent the spectroscopic values while the dark or shaded circles are used to mark experimental values obtained by calorimetric,[20] adiabatic expansion,[21] velocity of sound,[22] and explosion[23] methods. The experimental

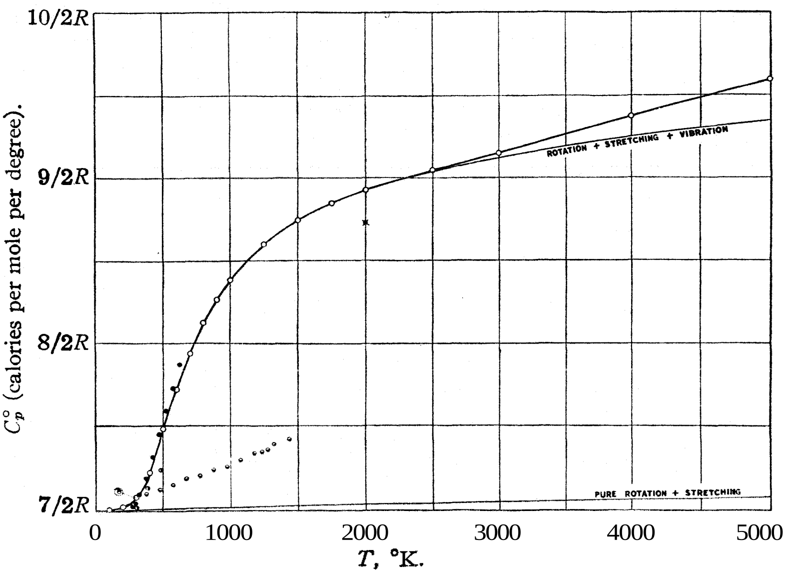

Fig. 5.—Heat capacity of gaseous oxygen: ○, Spectroscopic; ●, Henry; ◐, Eucken and Lude; 8, Partington and Howe; 9, Shilling and Partington; King and Partington; -●, Pier.

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(20) P. S. Henry, *Proc.* Roy. *Soc.* (London), **A133**, 492 (1931).

(21) (a) Eucken and Lude, *Z. physik. Chem.*, **5B**, 413 (1929); (b) Partington and Howe, *Proc. Roy. Soc.* (London), **A105**, 225 (1924).

(22) (a) Shilling and Partington, *Phil.* Mag., 6, 920 (1928); (b) King and Partington, *ibid.*, 9, 1020 (1930).

(23) Pier, *Z. Elektrochem.*, *16*, 536 (1909), recalculated by Lewis and Randall, THIS JOURNAL, 34, 1130 (1912).

values are included only for the sake of comparison since the spectroscopic values are the more reliable. The recent work of Henry[20] with a special type of flow calorimeter is in excellent agreement with the spectroscopic curve. The results obtained by the velocity of sound method,[22a,b] are obviously subject to some serious source of systematic error not detected by the investigators. We have omitted from the graph certain older[24] calorimetric measurements because of the crowded condition of the drawing.

It is noticeable that the heat capacity rises considerably above the classical $9/2R$ calories per mole per degree which, on the basis of the Equipartition Principle, is the limiting value for the heat capacity of a diatomic gas. This behavior, typical of other diatomic gases as well,[2] is a consequence of three factors which remove the gas from that condition hypothesized in the derivation of the Equipartition Principle. These factors are: (1) a variable moment of inertia, (2) the anharmonic character of the molecular vibration and (3) energy absorption by a change in electronic structure. In an effort to separate, more or less arbitrarily, the influences of these several factors, we have constructed the curves which are marked with special notations. Thus the curve marked "Pure Rotation + Stretching" was constructed by limiting our consideration to those quantum states which comprise the rotational levels of normal $^3\Sigma$ oxygen in its lowest, ($v = 0$), vibrational level. This yields a hypothetical rotational specific heat curve which, at 5000°K., exceeds rotational equipartition by some 0.06 calorie. This is directly a consequence of the "D" term in equation (2) and is attributable, physically, to energy absorption by the molecular stretching under the influence of centrifugal force, at high speeds of rotation. The curve marked "Rotation + Vibration + Stretching" was obtained by including all of the vibrational levels of normal $^3\Sigma$ oxygen.[25] Thus the difference between this and the previous curve represents the vibrational specific heat. For oxygen, the vibrational component attains its equipartition allotment at about 2500°K. and at 5000°K. exceeds this limit by about 0.30 calorie.

The inclusion of the $^1\Sigma$ electronic term, whose contribution to the specific heat becomes appreciable at about 2500°K., yields the complete specific heats, which are listed in Table III and are used to construct the heavy curve in Fig. 5. Although the numbers of molecules converted to the diamagnetic $^1\Sigma$ form are inconsiderable (*cf.* Table V) below 5000°K. the excitation energy is so large (37,000 calories per mole) in comparison with the other ways of internal energy absorption that the specific heat contribution is significant at the higher temperatures, and attains 0.25 calorie per mole per degree at 5000°K.

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(24) (a) Holborn and Austin, *Wiss. Abhand. physik. tech. Reichsanstalt*, *4*, 133 (1905); (b) Scheel and Heuse, *Ann. Physik*, **40**, *473* (1913).

(25) The reliable corrected approximation formulas used in the previous calculations (Ref. 2) were employed to minimize the labor.

Tables IV and V show the effect of temperature on the distribution of molecules among the various quantum levels available to molecular oxygen (*cf.* Fig. 3).

TABLE IV

ELECTRONIC AND ROTATIONAL DISTRIBUTION OF OXYGEN MOLECULES BELOW 10°K.

T, °K.	(K = 1) levels F_3	F_1	Fa	[illegible]	(K = 5) levels
0.025	99.9998	0.0002			
.050	99.71	0.29			
.075	96.63	3.37			
.100	89.2	10.8			
.125	79.7	20.3			
.150	70.6	29.4			
.175	62.8	37.2			
.200	56.3	43.7			
.25	47.1	52.9			
.50	29.5	70.2	0.3		
.75	24.4	74.4	1.2		
1.00	21.8	75.1	3.1		
2	17.1	71.6	11.3		
3	15.5	67.7	16.6	0.2	
4	14.1	64.6	19.9	1.4	
5	13.1	61.5	21.6	3.8	
6	12.4	58.2	22.3	7.1	
7	11.5	54.9	22.4	11.1	0.1
8	10.8	51.6	22.1	15.3	0.2
9	10.1	48.6	21.7	19.1	0.5
10	9.5	45.8	21.0	22.8	0.9

TABLE V

PERCENTAGE DISTRIBUTION OF MOLECULES AMONG THE VIBRATIONAL LEVELS OF THE NORMAL $^3\Sigma$ STATE OF OXYGEN, AND IN THE EXCITED $^1\Sigma$ STATE

T, °K.	298.1	400	500	600	700	800	900	1000
$^3\Sigma$, 0	99.94	99.62	98.83	97.54	95.80	93.73	91.47	89.06
$^3\Sigma$, 1	0.06	0.38	1.16	2.40	4.01	5.87	7.77	9.69
$^3\Sigma$, 2	0.00	0.00	0.01	0.06	0.18	0.38	0.69	1.10
$^3\Sigma$, 3			0.00	0.00	.01	.02	.06	0.13
$^3\Sigma$, 4					.00	.00	.01	.02
$^3\Sigma$ (5–∞)							.00	.00
$^1\Sigma$								

T, °K.	1250	1500	1750	2000	2500	3000	4000	5000
$^3\Sigma$, 0	82.90	76.95	71.46	66.51	58.09	51.29	41.18	34.03
$^3\Sigma$, 1	14.09	17.61	20.22	22.07	24.09	24.68	23.86	22.04
$^3\Sigma$, 2	2.47	4.13	5.85	7.46	10.14	12.03	13.96	14.39
$^3\Sigma$, 3	0.44	0.99	1.72	2.56	4.32	5.93	8.23	9.45
$^3\Sigma$, 4	.08	.24	0.52	0.89	1.87	2.95	4.89	6.24
$^3\Sigma$ (5–∞)	.02	.08	.23	.51	1.47	3.05	7.54	12.98
$^1\Sigma$	.00	.00	.00	.00	0.02	0.07	0.34	0.87

The distributions are calculated on the basis of the Maxwell–Boltzmann law of energy partition.[26]

By reference to these tables the changes which occur in the body of gas during the process of heat absorption are easily visualized. Below 0.02°K. substantially *all* molecules of oxygen are in a single quantum state—the F_3 form with the rotational quantum number $(K = 1)$—and the heat capacity is identical with that of a monatomic gas. Above 0.02°K. molecules attain to quantum states possessing higher energies and the energy absorbed in the process results in the appearance of specific heat associated with internal degrees of freedom. The first of these absorption processes corresponds to the transformation of molecules from the F_3 to the F_1 form of coupling without change in the rotational quantum number, and produces the first sharp maximum at about 0.12°K., where the ***rate*** of this transformation is greatest. The second, considerably broader, maximum at a little above 1°K., results from a similar transformation of a portion of the molecules to the F_2 coupling state, still without change in the rotational quantum number. Between 2 and 10°K. the specific heat, in excess of that due to translation, is due principally to excitation of molecules to the $(K = 3)$ rotational levels. As Table IV makes plain, the near attainment of rotational equipartition does not require a large distribution of molecules among the higher rotational levels. In oxygen, at 10°K., 76% of the molecules still remain in the $(K = 1)$ levels and less than 1% have attained the third set of rotational levels (with $K = 5$). Table V indicates the character of the absorption processes responsible for the specific heat components which enter at the higher temperatures.

The Entropy of Oxygen.—Table VI gives the entropy of oxygen for temperatures ranging from 1 to 5000°K. These values refer to the hypothetical ideal gaseous state at a pressure of 1 atmosphere and are expressed in calories per mole per degree.

TABLE VI

ENTROPY OF OXYGEN IN THE IDEAL GASEOUS STATE AT ONE ATMOSPHERE PRESSURE

T, °K.	S^0	T, °K.	S^0	T, °K.	S^0	T, °K.	S^0
1	11.780	90.125	40.686	700	55.314	1750	63.023
5	20.711	200	46.236	800	56.381	2000	64.203
10	25.390	298.1	49.018	900	57.342	2500	66.198
25	31.764	400	51.121	1000	58.214	3000	67.848
50	36.587	500	52.740	1250	60.099	4000	70.500
75	39.410	600	54.117	1500	61.674	5000	72.607

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(26) At very low temperatures an actual gas will obey the Bose–Einstein statistics rather than the Boltzmann statistics. However, this need concern us no more than the recognition that actual gases are subject to Van der Waals forces. Were we attempting to compare experimental data on the actual gas with our calculated values, it would be necessary to make corrections both for Van der Waals' imperfection and for quantum degeneracy, since our calculations apply to the hypothetical ideal gaseous state which, by definition, excludes both of these forms of imperfection. However, in this paper, we desire to know the results in terms of just such an ideal gas since the "standard state" of thermodynamic usage is customarily defined in terms of such a gas. For a further discussion of this point see Giauque, THIS JOURNAL, 52,4810 (1930).

The Free Energy.—In Table VII we give values of $-(F^\circ - E_0^\circ)/T$ for gaseous oxygen at a pressure of one atmosphere. Underscored values were calculated from the spectroscopic data. The remainder were interpolated by a graphical method.

TABLE VII

"FREE ENERGY" OF GASEOUS OXYGEN[27]

T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$
75	32.551	1150	51.770	3000	59.458
90.125	33.812	1200	52.095	3100	59.734
200	39.315	1250	52.408	3200	60.003
298.1	42 081	1300	52.712	3300	60.262
300	42.125	1400	53.286	3400	60.515
350	43.193	1500	53.826	3500	60.761
400	44.127	1600	54.334	3600	61.001
450	44.951	1700	54.814	3700	61.232
500	45.691	1750	55.045	3800	61.462
550	46.364	1800	55.270	3900	61.685
600	46.984	1900	55.702	4000	61.903
650	47.555	2000	56.117	4100	62.115
700	48.089	2100	56.512	4200	62.323
750	48.591	2200	56.890	4300	62.527
800	49.062	2300	57.254	4400	62.725
850	49.506	2400	57.603	4500	62.921
900	49.929	2500	57.939	4600	63.111
950	50.329	2600	58.264	4700	63.300
1000	50.715	2700	58.576	4800	63.484
1050	51.080	2800	58.880	4900	63.664
1100	51.431	2900	59.174	5000	63.840

Evaluation of the Limits of Error.—Below 1000°K., substantially all of the terms needed to evaluate the several sums employed in the present calculations lie within the range of energies covered by spectroscopic observations which the energy equations accurately reproduce. Even at 5000°K. the several higher vibration levels which make appreciable contributions to the sums are almost entirely represented in the observed bands. Thus only 0.15% of ΣA (cf. Ref. 2 for the significance of symbols), 0.7% of ΣB and 2.1% of ΣC were contributed by vibration levels whose energies were extrapolated by the accurate equation (1). As in nitric oxide, a considerably larger fraction of the rotational sums was contributed, at the higher temperatures, by rotation terms whose energies lay beyond

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[27] A few of these values differ slightly (by the order of 0.01 or 0.02 unit) from a preliminary table furnished to Clayton and Giauque and used by them in their calculation of the CO equilibria [Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932)]. Since the small effect which these changes would produce in their calculations lies well within other sources of error no corrections need be applied to their tables.

the spectroscopic observations. This is illustrated in Table VIII which shows: (1) the total number of rotational terms summed in the normal vibration level of the $^3\Sigma$, F_1 series, and (2) the number of these terms, starting with (K = 1), which contributed 90% of the totals of the respective sums. The actual spectroscopic data covered the first 13 rotational terms

TABLE VIII

THE NUMBERS OF ROTATIONAL TERMS WHICH CONTRIBUTED APPRECIABLY TO THE ROTATIONAL SUMS OF THE $^3\Sigma$, F_1 (v = 0) STATE

T, °K.	Total (all sums)	Terms contributing 90% of the respective sums		
		ΣA	ΣB	ΣC
1000	54	16	23	27
2000	67	23	31	36
3000	85	40	50	59

(to K = 25). It was thus necessary, at these higher temperatures, to employ equation (2a) to compute the energies of many rotational terms which lie beyond those observed experimentally. However, this does not constitute a serious source of error for equation (2a) reproduces the experimental data, both for ordinary oxygen and for the isotopic displacements, with an accuracy which approximates 0.01 cm.$^{-1}$ on the average[28] and the equation should extrapolate with considerable accuracy for several rotation terms beyond those which enter into the observed data. In order to set a reasonable limit to the inaccuracy which might enter through this extrapolation we have recalculated, at representative temperatures, the heat capacity, entropy and free energy on the supposition of a ± 50% error in the D constant of equation (2a). The changes thus produced are recorded in Table IX.

TABLE IX

ERRORS INTRODUCED BY A 50% ERROR IN THE CONSTANT OF THE QUADRATIC TERM IN EQUATION (2a)

T, °K.	C_p°	S°	$-\frac{F^\circ - E_0^\circ}{T}$
2000	0.000	0.004	0.002
3000	.000	.004	.003
5000	.000	.004	.003

A similar recalculation on the basis of a reasonable limit to the inaccuracy of the B constant of Table I produced changes much smaller than these. If we make some allowance for small inaccuracies in the B constants of the higher vibrational levels, in the vibrational frequencies and in the physical constants which are employed, it would appear that 0.02 or 0.03 calorie per mole per degree would cover the uncertainties in either heat capacities, entropies or free energies, even at 5000°K.

However, this statement must be modified to admit two sources of uncertainty, operative in the extreme regions of temperature, which involve

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(28) Birge, *Nature*, 134, 13 (1929).

neither the energy equations nor the physical constants used in the computations. The possibility of an error in the energy of the first F_3 rotational level, which would influence the magnitudes of the calculated values below 10°K., has already been discussed. The other source of uncertainty arises from the not unlikely possibility of the existence of a metastable $^1\Delta$ electronic term intermediate between the $^3\Sigma$ and $^1\Sigma$ states which are involved in the atmospheric bands (cf. Fig. 3). This level has been predicted, on theoretical grounds, by Mulliken[29] and by Hückel,[30] who estimates that the level lies about midway between the $^3\Sigma$ and $^1\Sigma$ terms. As this state has never been confirmed experimentally, we are unable to know certainly of its existence, or to evaluate accurately the contribution it would make to the results of the present calculations. However, we can estimate the approximate influence on the heat capacity curve at high temperatures should the term exist with the approximate energy hypothesized by Hückel. The effect would be to add what we might term a $^1\Delta$ component to the heat capacity curve. Such a component would become effective at about 1250°K., and at 2500°K. would have attained the approximately 0.25 calorie which the $^1\Sigma$ component attains at 5000°K. The $^1\Delta$ contribution would continue to rise above this value and would ultimately attain a maximum, followed by a gradual decline, in much the same manner as exhibited by the electronic coupling energy contributions which appear in the curve below 3°K. For either the $^1\Delta$ or $^1\Sigma$ levels, however, the maximum would not appear until very high temperatures were reached. The presence of the $^1\Delta$ term would also produce an increase in the numerical values of Tables VI and VII, at high temperatures, but the influence would be relatively less than for the heat capacity.

Between about 10 and 1200°K. the values recorded in Tables III, VI and VII should be fully as reliable as previous considerations have indicated. That is, an accuracy of ±0.01 calorie per mole per degree, or better, should apply to any of these quantities, on the basis of the "International Critical Tables" values for the physical constants employed in the calculations.

It is improbable that, in addition to the $^1\Sigma$ state and the hypothetical $^1\Delta$ state, there can exist other electronic terms with excitation energies sufficiently low to influence our calculations. Should the existence of a $^1\Delta$ term be verified experimentally and its excitation energy be determined, together with its accompanying vibrational and rotational constants, it will be a small matter to amend our present calculations to include the contributions of this term. It is our intention to do this should the necessity arise. In conclusion, we wish to emphasize the fact that the future discovery of any quantum states which may now be unknowingly omitted

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(29) Mulliken, *Phys. Rev.*, **32**, 186 (1928).

(30) Hückel, *Z. Physik*, **60**, 442 (1930).

from our interpretation may lead to an ***increase*** of the numerical values of the accompanying tables, but that no such future discovery can lead to a ***decrease*** of these figures.

We wish to acknowledge a grant from the Graduate Council of the Ohio State University, which provided research assistance that has greatly aided us in this investigation. The completion of the calculations was also greatly facilitated through the use of an electric computing machine obtained by a grant from the National Research Council.

Summary

The spectroscopic interpretation of the oxygen molecule has been briefly summarized.

The heat capacity of molecular oxygen in the ideal gaseous state has been calculated for the temperature range 0.02 to 5000°K. The heat capacity curve shows two maxima below 2°K. These are due to transformations between closely related electronic forms of the normal molecule. The rotational component of the specific heat appears a little below 3°K. and attains rotational equipartition at about 10°K. The vibrational component makes its appearance at about 200°K., and passes the equipartition value at about 2500°K. At high temperatures the rotational component of the specific heat exceeds the equipartition value due to centrifugal stretching of the molecule and the vibrational component exceeds R calories due to the anharmonic character of the oscillations. At about 2500°K. an additional electronic component of the specific heat makes its appearance. This arises from the excitation of molecules into the $^1\Sigma$ electronic term of the "atmospheric" bands.

Tables are included which show the temperature distributions of oxygen molecules among the various rotational, vibrational and electronic levels.

The entropy has been calculated and tabulated for temperatures from 1 to 5000°K.

The "free energy," as represented by the quantity $-(F^\circ - E_0^\circ)/T$ has been evaluated from 75 to 5000°K., and tabulated in a fashion that permits easy interpolation.

The probable errors of the heat capacity, entropy and "free energy" calculations have been determined. Also the possible influences of a small error in the coupling energy of the lowest F_3 rotational state and of the existence of a $^1\mathrm{A}$ electronic state have been discussed. These uncertainties affect the calculations only at very low and at very high temperatures. Between 10 and 1200°K. the calculations are regarded as accurate to within ±0.01 calorie per mole per degree.

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The Dissociation of Oxygen to 5000°K. The Free Energy of Atomic Oxygen[1]

BY HERRICK L. JOHNSTON AND MARGERY K. WALKER

Knowledge of the extent to which the common gases are thermally dissociated can be of value in the interpretation of phenomena which relate to reaction kinetics, specific heats, gaseous conduction, etc. Direct measurement of the dissociation of the more stable gases is quite difficult due, at low temperatures, to the small magnitude of the effect and, at high temperatures, to numerous experimental difficulties. A new and highly accurate point of approach is now available for several gases, as a result of the recent developments in the fields of molecular and atomic spectra. The first extensive and accurate calculation of a gaseous dissociation, based entirely on spectroscopic data, was made by Giauque,[2] who calculated the dissociation of hydrogen for various temperatures between room temperature and 5000°K. The earlier experimental results of Langmuir[3] and of Langmuir and Mackay[4] were found to be in very satisfactory accord with the more accurate values derived from the spectroscopic data. The present paper presents the results of similar calculations for the dissociation of molecular oxygen between room temperature and 5000°K.

Thermodynamic Relationships.—The calculations make use of the relationships

$$\begin{aligned} -R \ln K &= AF^{\circ}/T \\ &= 2\left(\frac{F^{\circ} - E_0^{\circ}}{T}\right)_{O} - \left(\frac{F^{\circ} - E_0^{\circ}}{T}\right)_{O_2} + \frac{\Delta E_0^{\circ}}{T} \end{aligned} \qquad (1)$$

Here R is the molar gas constant, in calories; T, the absolute temperature; ln K, the natural logarithm of the dissociation constant; AF°, the free energy change which accompanies the dissociation of one mole of molecular oxygen in the hypothetical ideal gaseous state, at one atmosphere, into monatomic oxygen in the perfect gaseous state, at one atmosphere; the parenthetical quantities are the molal "free energies" of atomic and molecular oxygen, respectively; and ΔE_0° is the molecular heat of dissociation at the absolute zero. It, like the parenthetical terms, can be evaluated, in this instance, entirely from trustworthy spectroscopic data. In making the computations in the above equation the molal "free energies" for molecular oxygen are taken from Table VII of the previous paper.[5] The "free energies" of atomic oxygen are computed by us and are given in

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(1) Presented March 31, 1931, as part of the Symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

(2) Giauque, THIS JOURNAL, 52, 4816 (1930).

(3) Langmuir, (a) *Trans. Electrochem. Soc.*, 20, 225 (1911); (b) THIS JOURNAL, 34, 860, 1310 (1912); (c) ibid., 37, 417 (1915).

(4) Langmuir and Mackay, *ibid.*, 36, 1708 (1914).

(5) Johnston and Walker, *ibid.*, 66, 172 (1933).

Table II of the present paper, and the dissociation energy of oxygen, whose reliability is discussed in **a** later paragraph is taken to be 5.09 (±0.03) volts (equal to 117,350 (±700) calories per mole.)

The Free **Energy** of Atomic **Oxygen.**—Following equation (4) of a previous paper[6] the mold "free energy" of atomic oxygen in the hypothetical ideal gaseous state is given by the expression

$$\left(\frac{F^\circ - E^\circ_0}{T}\right) = 5/2R - 3/2R \ln T - R \ln \frac{RT}{P}$$
$$- 3/2\ R \ln 16 + 11.057 - R \ln \Sigma A \qquad (2)$$

Before we can evaluate the last term in this equation we must know the nature of the more stable quantum levels of atomic oxygen, their statistical weights and their relative energies.

The normal, or valence, level of the neutral oxygen atom is an inverted ^3P term?

The existence of metastable $^1D_2$ and $^1S_0$ terms, corresponding to considerably higher energies, has also been established[8] from the line spectra of neutral oxygen. Still other electronic states are known but we need not consider these because their energies are so great, compared to the normal ^3P term, that their influence in the present calculations is entirely negligible. Nor is there likelihood of the occurrence of unidentified levels of sufficiently low energy to influence our calculations, because the observed ^3P, ^1D and ^1S levels are in accord with the well-established theoretical relationships which connect the spectroscopic terms with the position of the element in the Periodic Table.[9]

The relative energies of these various atomic levels of oxygen are given in Table I, together with their respective statistical weights.

TABLE I

RELATIVE ENERGIES AND STATISTICAL WEIGHTS OF THE MORE STABLE QUANTUM STATES OF THE NEUTRAL OXYGEN ATOM

	Relative energies		
Term	Volts	Calories per mole	Statistical weight
$^3P_2$	0.000	*0*	*5*
	.020	*449.4*	3
$^3P_0$	.028	*644.5*	*1*
$^1D_2$	*1.957*	*45,096*	*5*
$^1S_0$	*4.168*	*96,039*	*1*

From this table ΣA, of equation (2), was evaluated by the relationship

$$\Sigma A = 5 + 3e^{-449.4/RT} + 1e^{-644.5/RT} + 5e^{-45,096/RT} + 1e^{-96,039/RT} \qquad (3)$$

This then permitted the evaluation of the molal "free energies" of mon-

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(6) Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

(7) Hopfield (a) *Nature*, **112**, 437 (1923); (b) *Phys. Rev.*, **21**, 710 (1923); (c) *Astrophys.* J., 59, 114 (1924); (d) *Phys. Rev.*, 37, 160 (1981).

(8) (a) Frerichs, *ibid.*, 36, 398 (1930); (b) Paschen, *Naturwissenschaften*, 18, 752 (1930); (c) Sommer, ibid., 18, 752 (1930).

(9) Cf. Ruark and Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co . New York, 1930, ch. IX and p. 326.

atomic oxygen by equation (2). These were evaluated for temperatures ranging from room temperature to 5000°K., and are tabulated in Table II.

TABLE II

MOLAL "FREE ENERGY" OF MONATOMIC OXYGEN IN THE IDEAL GASEOUS STATE

T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$
298.1	33.090	1250	40.616	3100	45.226
300	33.124	1300	40.817	3200	45.386
350	33.952	1400	41.196	3300	45.541
400	34.666	1500	41.549	3400	45.691
450	35.293	1600	41.877	3500	45.837
500	35.852	1700	42.186	3600	45.979
550	36.355	1750	42.333	3700	46.117
600	36.812	1800	42.476	3800	46.252
650	37.232	1900	42.751	3900	46.383
700	37.620	2000	43.012	4000	46.511
750	37.980	2100	43.259	4100	46.635
800	38.315	2200	43.494	4200	46.757
850	38.630	2300	43.719	4300	46.876
900	38.925	2400	43.934	4400	46.992
950	39.205	2500	44.141	4500	47.105
1000	39.470	2600	44.338	4600	47.216
1050	39.694	2700	44.529	4700	47.325
1100	39.960	2800	44.713	4800	47.431
1150	40.189	2900	44.890	4900	47.536
1200	40.407	3000	45.062	5000	47.643

This table is of use not alone in the immediate calculations but in equilibrium computations for any reaction in which monatomic oxygen is involved.

The Heat of Dissociation of Molecular Oxygen.—Birge and Sponer[10] obtained a value of 0.81 volt for the energy required to dissociate an excited $^3\Sigma_u^+$ oxygen molecule into atoms. Assuming that this dissociation was into normal atoms, Birge and Sponer thus obtained the value 7.05 volts for the dissociation of a normal molecule into normal atoms. A later theoretical treatment by Wigner and Witmer[11] showed that $^3\Sigma_u^+$ oxygen must dissociate into one normal atom and one excited atom in a $^1D_2$ level. The subsequent identification and measurement of this level[8b,c] led to the value of 5.09 (±0.03) volts for the dissociation of a normal oxygen molecule into normal atoms.[12]

This value is confirmed by a variety of independent determinations by other methods.[13]

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(10) (a) Birge and Sponer, *Phys. Rev.*, 29, 259 (1926); (b) Birge, *Trans. Faraday Soc.*, **25**, 707 (1929).

(11) Wigner and Witmer, Z. *Physik*, **51**, 859 (1928).

(12) Herzberg, Z. *physik. Chem.*, **10B**, 189 (1930).

(13) (a) Kassel, *ibid.*, **2B**, 264 (1929); (b) *Phys. Rev*, **34**, 817 (1929); (c) Mecke, Z. *physik. Chem.*, **7B**, 108 (1930); (d) Henri, Nature, **125**, 202, 275 (1930); (e) Kondvat'ev, Z. *physik. Chem.*, **7B**, 70 (1930); (f) Baxter, THIS JOURNAL, **52**, 3468 (1930); (g) Rodebush and Troxel, *ibid* . **52**, 3467 (1930); (h) Copeland, *Phys. Rev.*, **36**, 1221 (1930).

Even those values which differ from the spectroscopic value by eight or ten thousand calories constitute confirmations of the latter more accurate determination. This is a consequence of the fact that the only possible source of error in the spectroscopic value (beyond the very small error involved in the wave length measurements themselves) is associated with the point at which Birge and Sponer made their erroneous assumption—the nature of the dissociation products of the excited $^3\Sigma$ oxygen. If, for the sake of argument, we exclude the conclusions of Wigner and Witmer[11] one of the following alternatives would have to be accepted: dissociation into two normal atoms (the assumption of Birge and Sponer), dissociation into two $^1D_2$ atoms, or dissociation into one $^1D_2$ atom and one $^1S_0$ atom. These respective alternatives would lead to the following alternative heats of dissociation: 163,000 calories, 72,000 calories, 21,000 calories. Within each alternative the value would be accurate to within about 1000 calories. The several independent lines of investigation do not support any of these alternatives. So we may regard the heat of dissociation of normal oxygen molecules into normal oxygen atoms as fixed at 117,350 calories ± about 700 calories.

Since the spectroscopic energies correspond to molecular and atomic states whose term values are independent of temperature, the heat of dissociation from spectroscopic data is identical with the heat of dissociation at the absolute zero and so is identical with the ΔE_0° of our equation (1).

Equilibrium Constants and the Degree of Dissociation.—By means of equation (1) we have calculated equilibrium constants of the reaction $O_2 = 2O$. We have also calculated percentage dissociations for a total pressure of one atmosphere. These were calculated by the relationship

$$100\alpha = 100\sqrt{K/(K+4P)} \tag{4}$$

where P is the total pressure and 100α is the percentage dissociation. The results are tabulated in Table III. The limits of error are computed on the basis of an uncertainty of ±0.03 volt in the energy of dissociation.

TABLE III

DISSOCIATION CONSTANTS AND PERCENTAGE DISSOCIATIONS FOR MOLECULAR OXYGEN

(The Percentage Dissociations Are Computed for a Total Pressure of One Atmosphere)

T, °K.	$K = p_O^2/p_{O_2}$	Percentage dissociation
298.1	$(2.8 \pm 2) \times 10^{-81}$	$(2.6 \pm 1.2) \times 10^{-39}$
300	$(5.9 \pm 4) \times 10^{-81}$	$(3.9 \pm 1.7) \times 10^{-39}$
350	$(1.3 \pm 0.8) \times 10^{-68}$	$(5.7 \pm 2.3) \times 10^{-33}$
400	$(2.4 \pm 1.4) \times 10^{-59}$	$(2.5 \pm 0.9) \times 10^{-28}$
450	$(4.0 \pm 2.2) \times 10^{-52}$	$(1.0 \pm 0.3) \times 10^{-24}$
500	$(2.4 \pm 1.2) \times 10^{-46}$	$(7.8 \pm 2.3) \times 10^{-22}$
550	$(1.3 \pm 0.6) \times 10^{-41}$	$(1.8 \pm 0.5) \times 10^{-19}$
600	$(1.4 \pm 0.6) \times 10^{-37}$	$(1.9 \pm 0.5) \times 10^{-17}$
650	$(2.6 \pm 1.4) \times 10^{-34}$	$(8.1 \ast 2.2) \times 10^{-16}$

TABLE III (*Concluded*)

T, °K.	$K = p_O^2/p_{O_2}$	Percentage dissociation
700	$(2.0 \pm 0.8) \times 10^{-31}$	$(2.2 \pm 0.5) \times 10^{-14}$
750	$(6.1 \pm 2.3) \times 10^{-29}$	$(3.9 \pm 0.8) \times 10^{-13}$
800	$(9.2 \pm 3.3) \times 10^{-27}$	$(4.8 \pm 1.0) \times 10^{-12}$
850	$(7.7 \pm 2.6) \times 10^{-25}$	$(4.4 \pm 0.8) \times 10^{-11}$
900	$(4.0 \pm 1.3) \times 10^{-23}$	$(3.2 \pm 0.6) \times 10^{-10}$
950	$(1.4 \pm 0.5) \times 10^{-21}$	$(1.9 \pm 0.3) \times 10^{-9}$
1000	$(3.3 \pm 1.0) \times 10^{-20}$	$(9.1 \pm 1.5) \times 10^{-9}$
1050	$(5.7 \pm 1.6) \times 10^{-19}$	$(3.8 \pm 0.4) \times 10^{-8}$
1100	$(8.1 \pm 2.3) \times 10^{-18}$	$(1.4 \pm 0.2) \times 10^{-7}$
1150	$(8.9 \pm 2.4) \times 10^{-17}$	$(4.7 \pm 0.7) \times 10^{-7}$
1200	$(8.0 \pm 2.0) \times 10^{-16}$	$(1.4 \pm 0.2) \times 10^{-6}$
1250	$(6.0 \pm 1.5) \times 10^{-15}$	$(3.9 \pm 0.5) \times 10^{-6}$
1300	$(3.9 \pm 1.0) \times 10^{-14}$	$(1.0 \pm 0.1) \times 10^{-5}$
1400	$(1.1 \pm 0.3) \times 10^{-12}$	$(5.3 \pm 0.7) \times 10^{-5}$
1500	$(2.0 \pm 0.5) \times 10^{-11}$	$(2.2 \pm 0.2) \times 10^{-4}$
1600	$(2.5 \pm 0.5) \times 10^{-10}$	$(8.0 \pm 0.9) \times 10^{-4}$
1700	$(2.4 \pm 0.5) \times 10^{-9}$	$(2.4 \pm 0.2) \times 10^{-3}$
1800	$(1.7 \pm 0.4) \times 10^{-8}$	$(6.6 \pm 0.6) \times 10^{-3}$
1900	$(1.0 \pm 0.2) \times 10^{-7}$	$(1.6 \pm 0.2) \times 10^{-2}$
2000	$(5.15 \pm 0.9) \times 10^{-7}$	$(3.6 \pm 0.3) \times 10^{-2}$
2100	$(2.21 \pm 0.3) \times 10^{-6}$	$(7.5 \pm 0.7) \times 10^{-2}$
2200	$(8.31 \pm 1.2) \times 10^{-6}$	0.14 ± 0.01
2300	$(2.79 \pm 0.4) \times 10^{-5}$	0.26 ± 0.02
2400	$(8.47 \pm 1.2) \times 10^{-5}$	0.46 ± 0.03
2500	$(2.36 \pm 0.3) \times 10^{-4}$	0.77 ± 0.05
2600	$(6.05 \pm 0.8) \times 10^{-4}$	1.23 ± 0.1
2700	$(1.45 \pm 0.2) \times 10^{-3}$	1.91 ± 0.1
2800	$(3.28 \pm 0.4) \times 10^{-3}$	2.86 ± 0.2
2900	$(7.00 \pm 0.8) \times 10^{-3}$	4.16 ± 0.2
3000	$(1.42 \pm 0.2) \times 10^{-2}$	5.95 ± 0.3
3100	$(2.75 \pm 0.4) \times 10^{-2}$	8.27 ± 0.4
3200	$(5.13 \pm 0.5) \times 10^{-2}$	11.3 ± 0.6
3300	$(9.20 \pm 0.9) \times 10^{-2}$	15.1 ± 0.9
3400	0.160 ± 0.02	19.6 ± 0.7
3500	0.268 ± 0.03	25.1 ± 1.2
3600	0.438 ± 0.04	31.4 ± 1.3
3700	0.698 ± 0.05	38.6 ± 1.6
3800	1.08 ± 0.09	46.2 ± 1.7
3900	1.65 ± 0.15	54.0 ± 1.8
4000	2.45 ± 0.2	61.7 ± 1.7
4100	3.58 ± 0.3	68.7 ± 1.5
4200	5.14 ± 0.4	75.0 ± 1.4
4300	7.24 ± 0.6	80.2 ± 1.1
4400	10.1 ± 0.8	84.6 ± 1.0
4500	13.8 ± 1.1	88.0 ± 0.7
4600	18.6 ± 1.4	90.7 ± 0.5
4700	24.8 ± 1.8	92.9 ± 0.5
4800	32.7 ± 2.3	94.4 ± 0.4
4900	42.7 ± 3	95.6 ± 0.3
5000	55.4 ± 4	96.6 ± 0.2

This uncertainty, although small, entirely masks the small errors which may exist in the $-(F^\circ - E_0^\circ)/T$ values which are involved. A modification of this statement must be made for the five or ten highest temperatures in order to allow for the not improbable existence of a $^1\Delta$ molecular level.[14] We have estimated the possible effect that would be produced by the existence of the $^1\Delta$ level, by recalculating equation (1) for a few representative temperatures with the molecular "free energies" modified by inclusion of the contributions that would result from a singlet level about half way between the normal $^3\Sigma$ and the excited $^1\Sigma$ levels of molecular oxygen. The results of this recalculation are given in Table IV.

TABLE IV

DISSOCIATION CONSTANTS AND PERCENTAGE DISSOCIATIONS RECALCULATED WITH THE INCLUSION OF A HYPOTHETICAL $^1\Delta$ LEVEL IN MOLECULAR OXYGEN

T. °K.	K	Percentage dissociation
2000	5.14×10^{-7}	3.6×10^{-2}
2500	2.34×10^{-4}	0.77
3000	1.40×10^{-2}	5.92
4000	2.37	61.0
5000	52.6	96.4

The comparatively large specific heat contribution which the $^1\Delta$ term would make at high temperatures[5] is a result of the large quantity of energy absorbed by the few molecules which attain the $^1\Delta$ level. The contribution of the hypothetical $^1\Delta$ term to the "free energy," and hence to equilibria, is less significant because, in the latter case, the magnitudes of the energy play no part, except as they influence the statistical distributions.

The literature contains no reference to any direct determinations of the thermal dissociation of gaseous oxygen. From consideration of the energy losses of a tungsten filament in air, Langmuir made the observation[8a,b] that in the neighborhood of 2400°K. oxygen must be either largely dissociated into atoms or associated into ozone. From a consideration of the phenomena which occur in an electric arc in air, Karrer[15] concluded that oxygen must be partly dissociated at the temperature of the arc. Jenckel[16] measured the heat losses of a glowing Nernst filament in oxygen, as well as in nitrogen, and attempted to interpret his results in terms of dissociation of the oxygen. The latter quantity was computed from thermochemical data by means of an approximation formula. Jenckel's experimental results are not suitable for direct evaluation of the degree of dissociation.

The dissociation constants and percentage dissociations calculated in the present paper should be reliable, within the limits set in Table III, for use in all problems which involve the dissociation of oxygen.

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(14) For discussion of this point see Ref. 5.

(15) Karrer, *Trans. Am. Electrochem. Soc.*, *48*, *223* (1925).

(16) Jenckel, *Z. physik. Chem.*, **155A**, **100** (1931).

The completion of these calculations has been greatly aided by the use of an electric computing machine provided by a grant of the National Research Council. We also wish to acknowledge a grant from the Graduate Council of The Ohio State University, which provided research assistance.

Summary

Accurate values for the dissociation constants of molecular oxygen have been calculated for the temperature interval 298.1 to 5000°K. The calculations are based upon a thermodynamic treatment of reliable spectroscopic data.

Accurate values of the percentage dissociation at a total pressure of one atmosphere have also been calculated between 298.1 and 5000°K. The dissociation attains 1% at a temperature between 2500 and 2600°K. and, at 5000°K., the molecules are dissociated to the extent of 96.6 ± 0.2%.

The "free energy" of monatomic oxygen, as represented by the quantity $-((F^{\circ} - E_0^{\circ})/T)$, has been evaluated from 298.1 to 5000°K., and tabulated in a fashion which permits easy interpolation.

The possible inaccuracy introduced through the omission of a probable 'A electronic state of molecular oxygen has been discussed. At 5000°K. the uncertainty thus introduced cannot change the calculated percentage dissociation by more than about 0.2 of one per cent. Below 4000°K. the influence of the hypothetical $^1\Delta$ level is practically negligible. It is pointed out that the influence of a hypothetical $^1\Delta$ level cannot appreciably modify the values of the molecular free energy function for use in other equilibria which involve molecular oxygen.

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Spreading of Liquids on Solid Surfaces. The Anomalous Behavior of Fatty Oils and Fatty Acids with Experiments Leading to a Tentative Explanation

BY RONALD BULKLEY AND GEORGE H. S. SNYDER

Introduction

The accepted theories of spreading are supported by ample experimental evidence for the case of one liquid spreading upon the surface of another. For example, the known interfacial and surface tension relations lead to the expectation that fatty oils and fatty acids will possess a more marked spreading tendency on water than will hydrocarbons and well-refined mineral oils. This expectation is realized experimentally.

For the spreading of liquids on solids, however, the current theories are not well substantiated by experimental data. Indeed, for many liquid–solid systems there would appear to be a conspicuous, but heretofore overlooked, disagreement between theory and experiment. While the surface tension of solids and their interfacial tension against liquids cannot be measured, there is, nevertheless, considerable evidence to show that on metals as well as on water the fatty oils and fatty acids should possess a more pronounced spreading tendency than the mineral oils.

It is a matter of common observation that such is not the case. On smooth and clean metal surfaces a drop of olive oil or of oleic acid shows little tendency to flatten or spread, whereas liquid paraffin hydrocarbons and moderately viscous mineral oils spread readily and apparently without limit as long as any liquid substance remains.

It is the purpose of this paper to discuss some of the evidence for the genuine existence of the anomaly, and to suggest a tentative explanation based on experiments which will be described. The experiments are of further interest in that they show for the first time, as far as the authors are aware, the phenomenon of rupture of thin layers of liquid on a solid surface due to the instability created by an underlying adsorbed film of low surface energy. A similar effect for fatty and mixed oils on water is well known.

The Spreading Tendency

As early as 1805 Thomas Young[1] had considered the laws governing the spreading of liquids on solids, and had published his famous equation (1), describing the equilibrium of a drop of liquid on a solid surface.

$$T_m = T_{mo} + T_o \cos \theta \qquad (1)$$

Here the solid is represented by the subscript m, the liquid by o; T_m, T_{mo} and T_o are the surface tensions of the respective surfaces and interfaces, and θ is the angle of contact between the liquid and the solid.

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(1) Young, *Phil. Trans.*, 95, I, 65 (1805). *See* also "Works," i, p. 432.

In recent years Harkins and Feldman, Osterhof and Bartell and others[2] have formulated various spreading criteria which differ from each other in little except notation. If the tendency to spread be represented by S, then, ignoring the work of viscosity

$$S = T_m - T_{mo} - T_o \qquad (2)$$

for spreading on a solid surface.

The quantities T_m and T_{mo} cannot be measured, and it is consequently impossible to determine the numerical magnitude of the spreading tendency for any given instance of a liquid spreading on a solid surface. It is to be noted, however, that the common fatty oils and fatty acids differ but little in surface tension from mineral oils as a class. If there is any substantial difference, therefore, between the interfacial tensions of the fatty liquids against metals and the mineral oils against metals, that class of liquids which has the lower values of T_{mo} should possess the superior spreading tendency.

Evidence That the Interfacial Tension between Metals and Fatty Liquids Is Less than between Metals and Mineral Oils

(a) Preferential Adsorption.—In accordance with a well-known general principle, surfaces and interfaces tend spontaneously to assume a condition of minimum free surface energy. At an interface between a metal and a mineral oil containing fatty acid in solution, that constituent of the solution which lowers the interfacial tension by the greater amount should, therefore, become more concentrated than in the solution as a whole.

Fatty oils and fatty acids lower the static coefficient of friction between metal surfaces more than do mineral oils of the same viscosity. Moreover, a mineral oil containing only a small percentage of fatty acid lowers the friction almost as much as a straight fatty oil. The explanation generally accepted is that the fatty acids are preferentially adsorbed from their solutions in mineral oils by metallic surfaces. Other experimental evidence of a more direct nature will be presented later which leads to a similar conclusion, namely, that metal surfaces preferentially adsorb the fatty acids from solutions of the latter in mineral oil. On the principle stated above, the fatty acids must, therefore, reduce the surface tension of metals more than do mineral oils.

(b) Interfacial Tension between Oils and Mercury.—Harkins and Ewing, Wells and Southcombe, and Bhatnagar and Garner[3] have presented data showing that the interfacial tension between mercury and fatty liquids is considerably lower than between mercury and hydrocarbons or mineral oils. The differences reported are of the order of 20 to 50 dynes per cm. It is also shown that the addition of small percentages of fatty acid to a

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(2) Harkins and Feldman, THIS JOURNAL, 44, 2665 (1922): Osterhof and Bartell, J. *Phys. Chem.*, 34, 1399 (1930).

(3) Harkins and Ewing, THIS JOURNAL, 42, 2539 (1920); Wells and Southcombe. J. *Soc. Chem. Ind.*, 39, 51T (1920); Bhatnagar and Garner, *ibid.*, 39, 185T (1920).

mineral oil progressively lowers the interfacial tension between the oil and mercury.

Some rough preliminary measurements made during the course of the present investigation indicate that well-refined lubricating oils of a medium grade may have an interfacial tension against mercury 20 to 40 dynes per cm. higher than olive oil or than the same mineral oils containing 1 to 2% fatty acid.

The significance of these results to the question under discussion is obvious. Most solid metals probably have lower interfacial tensions against fatty oils and fatty acids than against mineral oils as is true for the case of the metal mercury. Moreover, the differences are not likely to be less than about 20 to 50 dynes per cm. As shown in Table I below, the difference between the surface tensions of the fatty liquids and the mineral oils is seldom greater than 2 or 3 dynes per cm. Clearly, on the basis of Equation (2) the fatty oils and fatty acids should manifest the more marked spreading tendency.

TABLE I

PREFERENTIAL WETTING OF POWDERS

o means powder wetted preferentially by oil; w means powder wetted preferentially by water

Test liquid	Viscosity, poises	Surface tension dynes/cm.	Zn	Cu	Fe	G
n-Tetradecane	...	..	w	w	w	..
Kerosene	...	26.2	w	w	w	w
Transformer oil	0.22	29.7	w	w	w	..
Light naphthene base oil	...	..	w	w	w	..
Turbine oil	0.53	30.0	w	w	w	w
Medium motor oil	1.33	31.0	w	w	w	..
Nujol	...	..	w	w	w	w
Turbine oil with 2% oleic acid	0.53	30.2	o	o	o	w
Turbine oil with 5% oleic acid	.52	30.0	o	o	o	..
Sperm oil	.28	31.8	..	..	..	..
Porpoise jaw oil	.32	29.1	o	o	o	..
Neat's-foot oil	...	..	o	o	o	..
Olive oil	.66	32.2	o	o	o	..
Lard oil	.90	32.0	o	o	o	..
Oleic acid	.37	31.5	o	o	o	w

(c) Preferential Wetting of Powdered Materials.—Davis and Curtis[4] have described a simple method of obtaining qualitative information on the relative interfacial tensions of powdered solids against water as compared to their interfacial tensions against organic liquids not miscible with water. The solid particles, completely immersed as a paste in one of the liquids, say liquid o, are brought into intimate contact with the second liquid, *w*, by stirring into the paste a quantity of the second liquid. The particles choose to remain in liquid o if, and only if $T_{mo} < T_{mw}$. If the reverse is

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[4] Davis and Curtis, Ind. *Eng. Chem., 24, 1137 (1932).*

true, that is, if $T_{mw} < T_{mo}$, then, on the principle of minimum energy, **the** particles will be preferentially wetted by liquid *w*, into which they will pass and remain.

Davis and Curtis applied the test to 15 different powdered solids, and used on each solid eleven fatty oils, two mineral oils and several other organic liquids. They found, with few exceptions, that the fatty oils displaced water from the surface of all the solids and that water in turn always displaced the mineral oils. No powdered metals were tested by Davis and Curtis, but in the present investigation their procedure has been applied to tests on powdered zinc, copper and iron, using the liquids listed in Table I. A powdered glass, G, such as is used in baked enamel coatings was also tested with several of the liquids. The results are given in tabular form below, together with the values for viscosity and surface tension of the liquids used here and in the spreading tests to be described later. The surface tension and the viscosity were determined at room temperature; the former with the du Noüy tensiometer with the aid of the correction factors given by Harkins and Jordan;[5] the latter with the Michell viscometer.

It will be observed that in every instance the fatty oils and the liquids containing the fatty acid displace water from the metal powders, and that water, in turn, displaces the petroleum oils. In other words, the metals are preferentially wetted in the order fatty liquid–water–petroleum oil, or

$$T_{mf} < T_{mw} < T_{mp} \qquad (3)$$

where *f*, w and *p* represent, respectively, fatty liquid, water and petroleum oil. While the tests are only of a qualitative nature, yet, from the interfacial tension measurements of oils against mercury and from the very clean-cut manner in which the oils displace or are displaced by water in the present experiments, it seems safe to state that the difference between T_{mf} and T_{mp} must be considerably greater than the slight differences between the surface tensions of the fatty liquids and the petroleum oils.

It is not possible to say from these experiments which of the two classes of organic liquids shows the lower interfacial tension against glass. The experiments described below indicate, however, that against this solid, also, the fatty materials show a lower interfacial. tension than the mineral oils.

(d) Deflocculation of Pastes.—An interesting experiment consists in mixing 10 or 20 g. of some very finely divided solid such as zinc oxide, powdered glass, powdered zinc, copper or iron into a paste with kerosene and then adding a drop of oleic acid. Only enough of the kerosene should at first be used as will wet the powder completely, yielding a paste so stiff that it can be molded into an upright prism. Considerably more kerosene can now be stirred in without changing the consistency noticeably, but if a single drop of oleic acid is added, the mixture, when stirred, becomes so thin that it will run far out over the plate.

(5) Harkins and Jordan, THIS JOURNAL, **52**, 1751 (1930).

For a similar experiment in which poppy seed oil took the place of oleic acid, Green[6] was able to show by photomicrographs that the pigment in the stiff paste was flocculated, whereas in the thin cream, which resulted from adding a drop of fatty material, the particles were evenly dispersed. The interpretation is that the fatty oil or fatty acid lowers the interfacial tension between solid and liquid to such an extent that no flocculating tendency remains. As long as a high interfacial tension prevails between solid and liquid the fine particles clump together to eliminate as much of the interface as possible.

The evidence of the experiments presented under (a), (b), (c) and (d), above, as well as others, such as heats of wetting, etc., which could be mentioned, is to the effect that the interfacial tension between metals and fatty oils and fatty acids is substantially less than between metals and petroleum oils. On the basis of the accepted theories of spreading, the spreading tendency of the fatty oils and fatty acids should then be correspondingly greater.

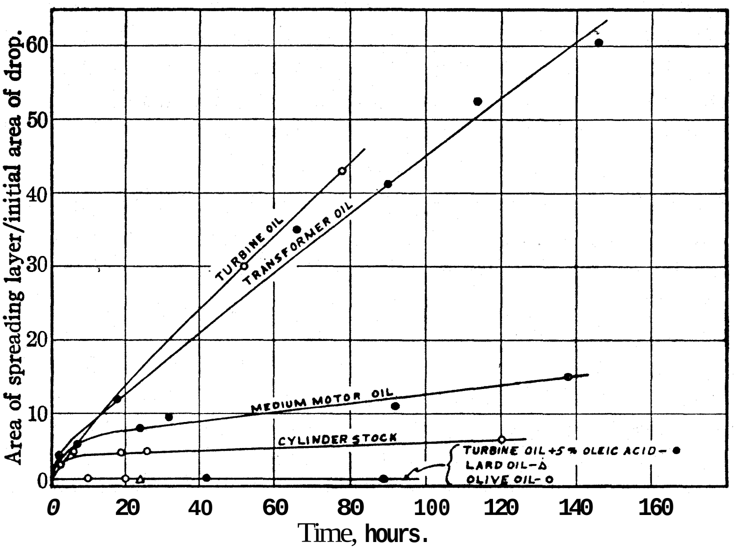

Fig. 1.—Spreading experiments on steel.

Spreading Experiments on Metal Plates

Figure 1 shows characteristic spreading graphs for droplets of various oils on brightly polished steel plates. In these graphs the ordinates represent the amount of spreading defined as the ratio of the area covered by the spreading layer at a chosen time to the initial area covered by the droplet, The initial area cannot be determined with precision, and a high degree of reproducibility is not obtained in duplicate experiments

(6) Green. *Ind. Eng. Chem.*, **15**, 122 (1923).

The test plates were polished to a mirror finish on wet broadcloth using chromium oxide as abrasive. They were kept level during the experiments and were protected from dust by suitable covers. An ample supply of fresh air was provided in all cases.

Figure 2 represents the behavior of several oils on polished surfaces of cadmium. It was not found possible to obtain as bright a polish on this metal as on steel, but, aside from this, the tests on cadmium and on steel were conducted under similar conditions. The shape of the curve for turbine oil is largely hypothetical as only the initial and final areas were measured.

In Fig. 3 the spreading liquid is a thin mineral oil. The non-spreading drop is olive oil. Both drops were initially of nearly the same size and both were put on the plate at the same time, about twenty hours before the picture was taken.

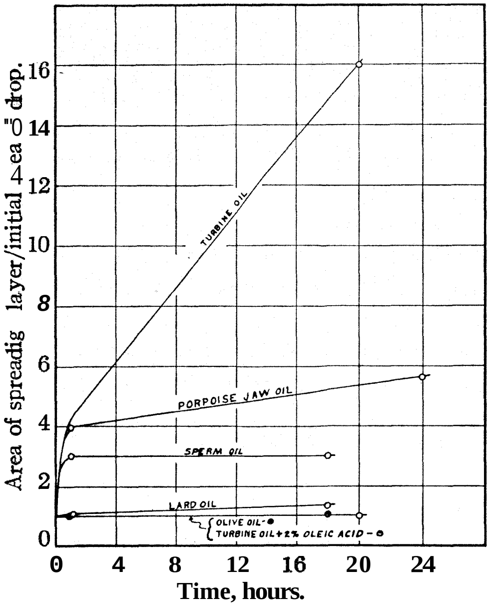

Fig. 2.—Spreading experiments on cadmium.

The behavior of mineral oils on a metal plate can be described by saying that each droplet flattens rapidly into a thin layer which seems to continue to spread indefinitely. In many instances the spreading has been observed to continue long after the layer has become so thin that several orders of color appear With an oil as volatile as kerosene the area covered reaches a maximum in a few hours, after which the layer disappears due to evaporation.

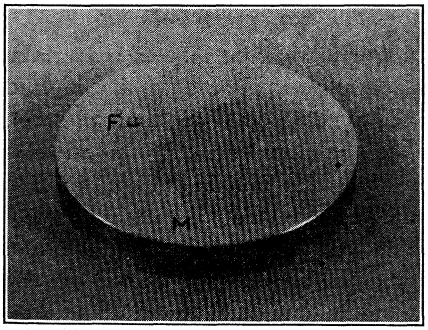

Fig. 3.—Relative spreading of fatty oil (F) and mineral oil (M) on steel plate.

Droplets of lard oil, olive oil and of mineral oils containing 5% or more of oleic acid spread only during the first few minutes after being placed on the plate. The lowest curves on Figs. 1 and 2 are representative. Porpoise jaw and sperm are exceedingly thin oils and have more marked spreading tendencies than other fatty oils. Mineral oils containing only 1 or 2% of fatty acid show about the same behavior as fatty oils on cadmium, but on steel and several other metals their behavior is peculiar and striking, and will be described in a later section.

Cadmium was chosen as one of the test metals because of its close relationship to mercury in the Periodic Table. If cadmium is affected in the same manner and to a similar degree as mercury by fatty and mineral oils, then the interfacial tension between cadmium and the three oils whose curves are shown at the bottom of Fig. 2 must be about 20 to 40 dynes per cm. less than the interfacial tension between cadmium and the turbine oil. The greatest difference in the surface tensions of the oils is 2.2 dynes per cm. By Equation (2), the lard oil, the olive oil and the turbine oil containing fatty acid should thus possess the greater spreading tendency. Experimentally these oils are observed not to spread to an appreciable extent. The spreading of liquids on solids seems, therefore, to be determined in many cases by factors other than the energy requirements.

Behavior of Fatty Acids and of Oils Containing Fatty Acids on Flat Plates

When a drop of oleic acid is placed on a clean polished surface of steel it apparently does not wet the plate at all, but can be rolled about in much the same manner as a drop of mercury.' A film of mineral oil spreading on the plate is halted abuptly at the invisible path along which the oleic acid has passed, thus giving evidence of the deposition of an exceedingly thin film on that part of the plate with which the drop has been in contact. The path of the drop can also be brought out strikingly to the eye merely by breathing on the plate when it is cool. Gentle etching with fumes from inorganic acids will likewise make the path of the drop visible.

The above effects seem to occur for a fairly wide variety of materials. They have been observed in this investigation for oleic acid, for melted capric, palmitic and stearic acids and for melted cetyl alcohol on steel, brass, babbitt, glass and mica. Several of the common fatty oils such as castor, lard and olive manifest a somewhat similar behavior, but to a less marked degree. Cadmium and platinum seem to be wetted in the ordinary sense of the word by all of the liquids mentioned above. This may be due, in part, to the difficulty of getting a sufficiently smooth polish on the surfaces of these metals.

Mineral oils which spread rapidly on ordinary metal surfaces seem to have no spreading tendency when placed on a metal surface which is covered with the invisible fatty acid film. The film thus seems to be similar to the neutralizing surface layer (epilame) described by Woog,[8]

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(7) This effect was first noticed by one of the authors (*G.* H. S. S.) in September, 1931.

(8) Paul Woog, *Compt. rend.*, 181, 772 (1925). See also "Contribution à l'Étude du Graissage," Delagrave. Paris. 1926.

but its thickness is probably only a small fraction of the thickness of the layers of stearic acid deposited by Woog's patented process. Indeed, there is good reason to believe that the drop of fatty acid leaves behind it only an adsorbed film, which is, therefore, perhaps only a few molecules in thickness. For instance, the surface may be rinsed several times in benzol without removing the film.

The effect of the adsorbed film in reducing the wettability of the metal surface by mineral oils goes further. This was demonstrated by rolling several drops of fatty acid across a plate, and then dipping the lower half of the plate into a beaker of mineral oil. When the plate was withdrawn the clean metal retained a relatively thick layer of oil for an indefinite period, but all the oil ran off those portions which the fatty acid drops had touched.

Another detail of interest was observed when a drop of oleic acid was placed just on the edge of a very shallow pool or layer of motor oil on a polished plate. The plate was level so there was no tendency for the drop to roll by gravity. It moved, nevertheless, of its own accord into and through the layer of oil, mixing with the portion in its path, and leaving behind on the steel only the adsorbed film with no visible trace of liquid (Fig. 4). For experiments in which the layer of mineral oil was very thin, the drop of fatty acid was often observed to traverse the entire width of the pool and then to turn about and recross in the opposite direction, wiping out a continuous path all the way.

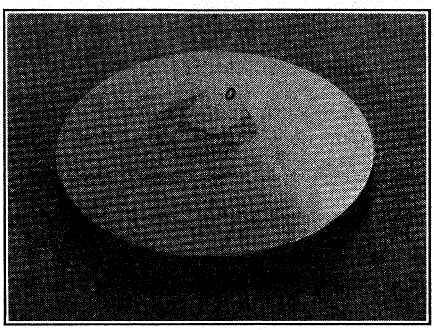

Fig. 4.—Action of a drop of oleic acid when placed at O on the edge of a spreading layer of mineral oil.

One additional group of observations may be described, after which an explanation of these phenomena will be attempted. When a drop of thin mineral oil containing 1 or 2% of oleic acid was placed on a polished steel plate it spread rapidly outward for a few minutes, at which time a hole appeared in the layer near its edge. This hole became elongated, expanding parallel to the circumference of the spreading layer. The main body of the oil pulled inward as the rupture progressed, until at last the oil was completely separated into two portions: a surrounding ring which continued to expand outward at a more rapid rate than the ordinary spreading, and an inner pool which contracted to a relatively small radius and then remained dormant (Figs. 5 and 6). On the metal surface between these two portions no liquid was visible. The surface was found to be covered with an adsorbed film similar in all respects to the one obtained from the pure acid.

On steel and on several other solid surfaces, solutions of various fatty acids in oil were found to behave in a somewhat similar manner. Some combinations were more active than others. Solutions of capric acid and palmitic acid in oil seemed to be more energetic than oleic acid in oil. Stearic acid solutions were almost inert. Fresh mica surfaces were somewhat more active than steel. For the more active combinations such as solutions of palmitic acid on steel or mica, the spreading layer sometimes appeared actually to fly to pieces on the surface, breaking up into numerous drops and droplets which moved rapidly about on the surface (Fig. 7). Each moving portion left in its wake a trail of adsorbed fatty acid on the metal surface.

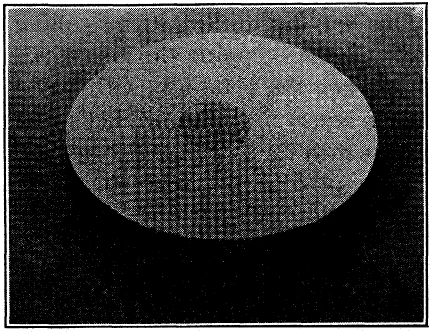

Fig. 5.—Ring commencing to break away (two per cent. of oleic acid in kerosene on steel).

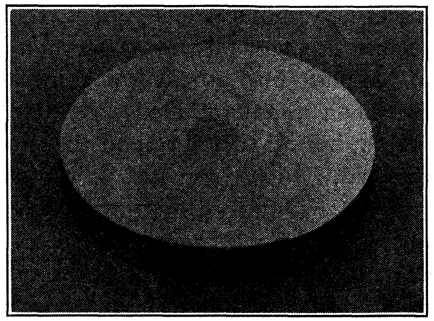

Fig. 6.—Later stage of ring mechanism (same view as Fig. 5 four minutes later).

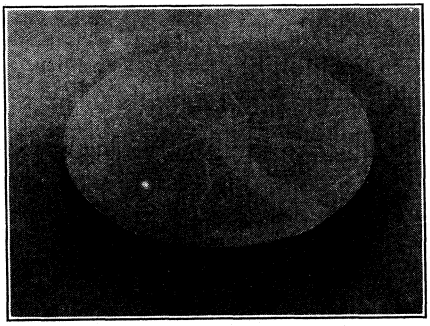

Fig. 7.—Configuration after explosive spreading (two per cent. of palmitic acid in kerosene on steel).

In some instances a drop as a whole was observed to move about. This behavior seems to be a characteristic of castor oil, the only non-compounded oil used, which was found to possess the type of activity mentioned here. On steel, drops of castor oil were observed to move slowly, leaving behind long thin arms of liquid. On fresh mica, the drop as a whole traveled about leaving no visible liquid behind.

The ability of a solid surface to produce the effects mentioned was found to be greatest immediately after the surface had been polished, and to decline rapidly with time of exposure to the laboratory atmosphere. This was evidently due to moisture or oil vapors, for when the surface was kept in a clean dry atmosphere the activity was found to have suffered only slightly after a period of sixteen hours.

The effect of concentration of the fatty acid in the oil was tried. From 0.1% up to saturation—about 2%—solutions of palmitic and capric acid in kerosene showed little change in behavior, except that at the lower concentrations more time was required before rupture occurred and the break started farther in from the edge. With oleic acid, which is more soluble in oils, it was possible to go to higher concentrations, and the results are considered to be of significance in arriving at an explanation of the non-spreading of fatty oils and fatty acids in general.

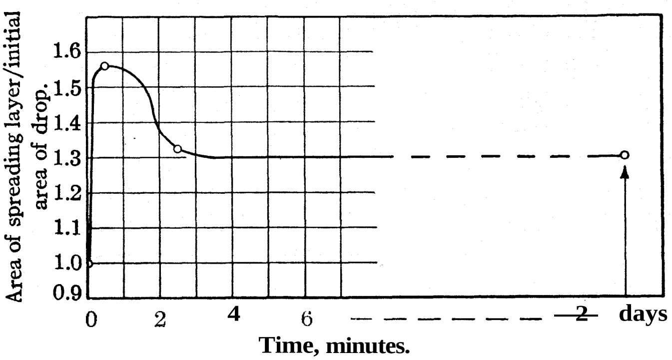

Fig. 8.—Spreading of a high viscosity compounded oil on steel.

At concentrations of oleic acid in kerosene less than one-half of 1% the initial rupture of the spreading layer was considerably delayed, and the ring which detached itself was wide. At 1% the rupture occurred sooner and closer to the edge of the spreading layer. At 2% the time before rupture was still less and the ring which detached itself was thinner than ever. At 5% the break often appeared to be just at the edge, and in several instances no visible ring could be observed to detach itself. In these cases a wave of contraction started at some point in the edge very shortly after the drop was placed, and spread around the periphery, the drop pulling itself inward as the wave progressed and then remaining completely dormant. At 10% no ring was ever seen, but the contraction of the drop immediately after placing was still visible. At higher concentrations this effect also disappeared, probably because it occurred too quickly to be observed.

For oils of higher viscosity, less fatty acid is required to make the rupture occur at or near the edge of the drop. For an oil of cylinder stock grade, 1% of oleic acid may be sufficient to produce a visible contraction of the drop after an initial period of spreading, without the appearance of any visible fringe or ring. Figure 8 is plotted from measurements made on such a drop with a cathetometer.

Relation of the Experimental Results to the Non-Spreading of Fatty Oils and Fatty Acids

Certain similarities exist between the behavior of fatty acids and fatty oils on water and their behavior on metals as described above.

Oleic acid spreads rapidly on the surface of clean water to give a layer of visible thickness, which at once gathers itself back up into a drop. The water is left covered with an adsorbed film which reduces the surface tension to a low value. The regathering of the bulk of the material into a drop comes about as a consequence of the low surface tension of the water when covered with such a film. Oleic acid does not spread of its own accord on a polished plate, but if it is forced to spread into a thin layer by mechanical means it will at once gather itself back up into a drop when the applied force is removed. Moreover, the area with which it has been in contact will remain covered with an adsorbed film.

The surface energy of the metal so covered will be low, as in the case of water. The value will be considerably less than that of clean metal and substantially less than that of metal covered with mineral oil. This was demonstrated for the case of metal powders and mercury in a previous section; the experiments describing the behavior of fatty acids and of oils containing fatty acids on flat plates confirm the essential correctness of this view. For instance, mineral oils will not spread on or readily adhere to the surface of metal covered with the adsorbed film. The fatty acid itself will not wet such a surface as shown by the rolling effect and the gathering into a drop. Again, when a drop of oleic acid travels of its own accord through a thin layer of mineral oil on a polished plate, and removes the oil from the surface, it is believed that the driving power responsible for such behavior is the considerable lowering of the surface energy of the metal which occurs when the mineral oil is replaced by fatty acid.

When mineral oils containing a small amount of fatty acid spread and rupture on solid surfaces the behavior is similar, and the cause of rupture is the same as when the spreading of such liquids takes place on water, The phenomena are well known for spreading on water and mercury; they have been described often, and have been beautifully illustrated by Beilby and by Devaux.[9] Therefore, only a brief discussion of the main features as applied to spreading on solids will be given here.

When a drop of petroleum oil containing some fatty acid is placed on a polished plate, the petroleum portion spreads in its normal manner; the fatty acid is preferentially adsorbed on the solid surface, and lowers the interfacial tension between solid and liquid to such an extent that a condi-

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(9) Sir George Beilby, "Aggregation and Flow of Solids," Macmillan and Co , London, 1921 Henri Devaux, *Kolloid-Z.*, 68, 129 (19.32).

tion of unstable equilibrium arises. The reason for this instability is comprised in the principles underlying Young's equation (1). It is perhaps sufficient merely to state in words that on an area of low surface energy the stable configuration for a small portion of liquid is not that of an extended film but that of a drop. At a certain minimum thickness of liquid layer, rupture therefore occurs. Any portion of oil in the midst of an area covered with the adsorbed film can only pull itself together into a drop; this is the situation for all the oil when the underlying substance is water or mercury. For spreading on solids, however, not all of the surface has been contaminated when rupture occurs, and the oil in contact with clean metal therefore continues to spread outward.[10]

A mechanism which may be responsible for the non-spreading of fatty oils and fatty acids is suggested by the experiments with kerosene containing varying percentages of oleic acid. For low concentrations the adsorbed film between the oil and metal seems to require more time to become organized completely than for high concentrations. It may be supposed that this film commences to form when the drop first touches the metal, and that it grows outward at a rate which is some direct function of the concentration of fatty acid. At low concentrations, therefore, not only will the rupture be delayed more than for high concentrations, but, when rupture is imminent, the advancing edge of the liquid layer will in general be farther away from the region in which the probability of rupture is the greatest. The break will occur closer and closer to the edge as the concentration is increased, until the ring which spreads outward becomes too thin to be seen. At very great concentrations it may be only of molecular dimensions. In all cases, however, the oil on the inward side of the rupture is pulled further inward by surface tension when rupture occurs, and is prevented from exhibiting any further spreading tendency by the surrounding area of metal of low surface energy.

This has been observed to be the mechanism of the non-spreading of mineral oils containing moderately high concentrations of oleic acid. The same explanation may be assumed for fatty oils and fatty acids if there exists in such liquids a small amount of a less active but spreading ingredient which permits the functioning of the mechanism described. Even for pure fatty acids a similar view can be held by considering the molecules as requiring at least a short time to become oriented on the surface. The ring which would be pictured as detaching itself in such a case would be a ring of unoriented molecules which would rapidly exhaust its substance in covering the metal surface to a very short distance beyond the edge of the drop.

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(10) The ring or droplets which result from the rupture of the original layer move faster than the ordinary spreading rate, prohably because the forces of surface tension roll the liquid up from the rear as fast as it spreads outward in the front. There is thus always maintained a hydrostatic head many times greater than that which is present in a normally spreading layer of oil.

The situation presented is somewhat curious. It might be said that mineral oils spread mainly because they reduce the surface tension of solids to a low value. With regard to fatty oils, fatty acids and mineral oils containing relatively large amounts of fatty acids, it becomes necessary to state that they fail to spread although they reduce the surface tension considerably more.

The paradox is adequately explained, for the case of the solutions of oil and fatty acid, by the ring mechanism which is easily and directly observed. For pure fatty oils and fatty acids the same mechanism suggests itself as a possible and reasonable explanation, although here other factors may have to be considered, especially for such materials as possess an appreciable vapor pressure. A high concentration of oleic acid vapor effectually prevents the spreading of mineral oils on a steel plate initially clean, presumably by condensing as an adsorbed film and lowering the surface tension of the metal. It seems likely that the condensation of vapor from a drop of oleic acid or fatty oil onto the immediately adjacent surface might similarly prevent the spreading which would be predicted for such a drop from energy considerations alone.

Adam[11] has suggested that the mechanism of spreading of a liquid layer on solids is the evaporation of the spreading material near its edge, followed by recondensation on the solid surface. The question might reasonably be asked as to how one and the same mechanism could produce spreading in the case of mineral oils, and prevent it in the case of fatty liquids. The probability that this situation actually prevails seems not to be great, but its possible existence may be admitted for the time being.

The answer to the above question would then seem to be that in the case of the fatty liquids the surface tension of the metal is reduced to such a low value by the condensed film as to make a liquid layer thereon unstable. If a layer thick enough to have the properties of a liquid should build up for a short distance beyond the drop, this layer would at once contract inward by reason of its own surface tension, and because of the low surface energy of the adjacent metal which, in the meantime, would have become covered with an adsorbed film.

An equally acceptable and perhaps simpler view is that when a liquid spreads, the liquid flows outward as liquid at the margin of the spreading layer, under the strong attractive influence of the solid surface molecules. If this point of view is adopted, the question discussed above does not present itself.

Regardless of what may be the mechanism of spreading, there can be little doubt that, in the case of fatty oils and fatty acids where the expected spreading fails to occur, the reason for the non-spreading is to be found in the fact that the surface energy of the metal surrounding the drop is re-

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(11) Adam, "The Physics and Chemistry of Surfaces," Oxford. 1930.

duced to such a low level as to make a liquid layer on the metal unstable. This reduction in surface energy is brought about either by the ring mechanism described in this paper, by the condensation of vapors in advance of the spreading layer or, perhaps, by a combination of both. Mineral oils and mineral oil vapors also reduce the surface energy, but not to a sufficient extent to make a thin liquid layer on the metal unstable.

Other Suggested Explanations.—The literature seems to contain no previous mention of the anomaly of the non-spreading of the fatty oils and fatty acids, and there are consequently to be found but few suggestions of a helpful nature as to its cause. Harkins and Feldman[2] are of the opinion that practically all organic liquids should spread readily on all clean metal surfaces because many such liquids spread readily on water, and "since the free surface energy of solids is in general much higher than of liquids, and since in general the interfacial tension is less than that of the surface tension by a greater amount." These authors suggest that cases of non-spreading of liquids on solids are to be explained by the presence of impurities on the surface which lower the free surface energy.

The arguments set forth in the present paper constitute further substantiation of the view of Harkins and Feldman that, on the basis of energy considerations alone, organic liquids should spread on clean solid surfaces. The presence of impurities on the surface, however, seems inadequate to explain the non-spreading of fatty oils and fatty acids. It is difficult to understand, for instance, what the nature of the contaminant could be which would interfere so slightly with the spreading of mineral oils on metal plates and at the same time entirely prevent the spreading of the fatty liquids which are possessed of the superior spreading tendency.

Moreover, platinum can be cleansed of organic contaminants very thoroughly by heating to incandescence, and glass can be brought to a comparable condition of cleanliness with the aid of strong acids. The spreading behavior of mineral oils and of fatty oils and fatty acids on surfaces so cleansed is, nevertheless, qualitatively the same as on the metal surfaces used throughout this investigation. In general the behavior is the same also on surfaces of mica freshly exposed by cleavage.

A test which is generally recognized as a delicate one for detecting minute amounts of contaminants on a solid surface is to see how well the surface retains a film of water. All the experiments described in the present papers were made on surfaces which were clean in the sense that they were capable of being wetted perfectly by water.

Woog's[8] suggestion as to the reason for the non-spreading of fatty oils is more in keeping with the experiments described in this paper, although it seems to have been made on the strength of meager evidence. No consideration is given to the energy relations involved, and there is no mention of the fact of an anomaly. His description of the manner in which drops of mineral oil containing fatty acid spread at first and then contract into drops is similar to some of the effects described in this paper (Fig. 8). If any rings separated from the drops in his experiments he apparently did not observe them. This may account for his failure to suggest any suitable mechanism for the formation of the zone of oriented molecules which he postulates as surrounding the drops.

Trillat and Cuypers[12] have quoted Woog's explanation without substantial modification.

Summary

Several lines of experimental evidence are described in support of the view that the interfacial tension between metals and petroleum oils is substantially greater than between metals and fatty oils or between metals and fatty acids.

The energy requirements for spreading on solids being the same as for spreading on liquids, the fatty oils and fatty acids should spread more readily than mineral oils on metal surfaces.

Experimentally, fatty oils and fatty acids spread little or not at all while mineral oils spread apparently without limit. The non-spreading of the fatty liquids must, therefore, be regarded as anomalous.

The higher fatty acids do not wet polished metal surfaces in the ordinary sense, but roll about freely. They deposit an adsorbed film on the surface which reduces the surface energy to a low value.

Thin layers of mineral oil containing fatty acids rupture spontaneously on metal surfaces. The explanation is the same as when a similiar phenomenon occurs on water, namely, the formation of an underlying film of low surface energy. Thin layers are unstable on areas of low surface energy.

Fatty oils and fatty acids are prevented from spreading on metal surfaces by the great reduction in the surface energy of the metal which is brought about to some distance in advance of the spreading layer by the breaking away of an expanding ring or by the condensation of vapors.

PAULSBORO, NEW JERSEY

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[12] J. J. Trillat, *Metallwirtschaft*, 4, 101 (1928); Paul Cuypers, *Deut. Uhrmacher Z.*, Nos. 35, 36, 37 (1927).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING,
CARNEGIE INSTITUTE OF TECHNOLOGY]

The Systems (I) Diphenyl–Diphenylamine, (II) Diphenyl–Benzophenone and (III) Benzophenone–Diphenylamine[1]

BY H. HOWARD LEE AND J. C. WARNER

This investigation was undertaken for the purpose of determining the freezing point-composition diagrams for the binary systems (I) diphenyl–diphenylamine, (II) diphenyl–benzophenone and (III) benzophenone-diphenylamine. The system benzophenone–diphenylamine was investigated by Giua and Cherchi[2] but their results are evidently in error over a considerable range of composition and we have consequently reinvestigated the entire system. Each of the three compounds contains two phenyl groups. Diphenyl is non-polar but benzophenone and diphenylamine possess electric moments of considerable magnitude. It was therefore considered of interest to compare actual solubilities to ideal solubilities in these systems.

Materials.—The chemicals were Eastman's "Highest Purity" grade. The diphenyl was purified by crystallization from alcohol, washing with ether and drying in an oven at 100°. The diphenylamine and benzophenone were distilled under reduced pressure. In each case recrystallization or redistillation was continued until no further change in melting point was observed. The melting points of the compounds used in the investigation are compared to the "International Critical Tables" values in Table I.

TABLE I

	Melting point, °C.		Heat of fusion,[3]
	Our material	I. C. T.	g. cal./mole
Diphenyl	69.0	69.0	4020
Diphenylamine	52.8	53.0	4260
Benzophenone	47.7	48.5	4290

The agreement in melting points is good except for benzophenone. It seems certain that the "I. C. T." melting point for benzophenone is in error since any number of recrystallizations or redistillations failed to yield a product of melting point higher than 47.7°. Furthermore, none of the seven reported investigations on binary systems with benzophenone[4] as one constituent shows a melting point for pure benzophenone above 47.7°.

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[1] This paper is based on a thesis submitted by H. Howard Lee to the Graduate Committee of the Carnegie Institute of Technology in partial fulfilment of the requirements for the degree of Master of Science.

[2] Giua and Cherchi, *Gazz. chim. ital.*, 49, II, 264 (1919).

[3] "International Critical Tables," Vol. V, p. 134.

[4] "International Critical Tables," Vol. IV.

Temperatures were measured with 100° thermometers graduated in tenths of a degree. They were compared to a thermometer of the same type which had been calibrated by the Bureau of Standards. Correction for emergent stem was always made when the correction was equal to, or greater than, the experimental error.

Experimental

Weighed samples in test-tubes (15 mm. diameter) were placed in larger test-tubes which were immersed in a water-bath. The melt was allowed to cool with the bath, the temperature difference between the bath and the sample ranging between a few tenths of a degree and several degrees depending upon the particular sample and the temperature at which observations were made. The samples were well agitated during cooling by a glass stirrer which encircled the thermometer stem. When undercooling occurred, the cooling curves were projected back to intersect with the liquid cooling curve to obtain a more accurate primary crystallization temperature. With some samples, particularly those containing high percentages of benzophenone or diphenylamine, undercooling was very marked in spite of vigorous agitation and inoculation. In such cases, the results obtained from cooling curves were checked by thermostating samples to determine the temperature at which the solid phase disappeared.

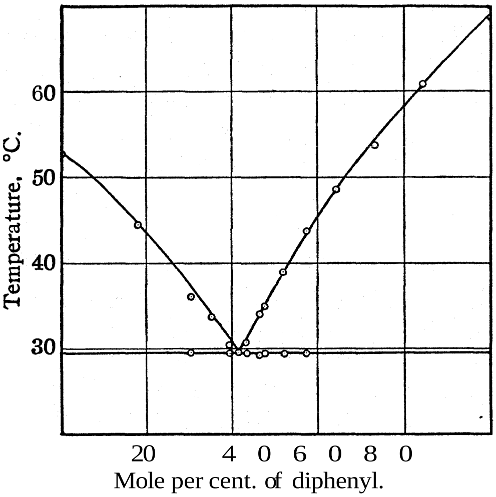

Fig. 1.—Diphenyl–diphenylamine.

(I) **Diphenyl–Diphenylamine.**—The freezing point–composition diagram for this system is shown in Fig. 1. The diagram is based upon the data in Table II.

A sample having the eutectic composition (41.7 mole per cent. diphenyl) indicated by the intersection of the liquidus curves solidified at 29.6'. This is in good agreement with the average final solidification temperature of 29.5'. Assuming ideal solution behavior and constant heats of fusion (see Table I), the calculated eutectic temperature is 26.5' and the eutectic composition is 43.8 mole per cent. diphenyl. The solubility of each constituent in the other is therefore less than the ideal solubility. This should be expected since one component is polar and the other non-polar.

Primary crystals of diphenyl which were separated from the liquid above the eutectic temperature melted sharply at 68.8°. Similarly obtained crystals of diphenylamine melted sharply at 52.8'. Hence there is no appreciable solubility of the constituents in each other in the solid state.

TABLE II

Mole per cent. diphenyl	Initial cryst. temp., °C.	Final solidification temp., °C.
0.0	52.8	52.8
18.0	44.5	
30.5	36.0	29.6
35.4	33.6	
39.7	30.3	29.5
41.7 E	29.6	29.6
43.5	30.8	29.6
46.7	34.1	29.3
47.8	35.0	29.5
52.3	39.0	29.5
57.5	43.7	29.4
64.6	48.6	
73.2	53.7	
84.5	60.9	
100.0	69.0	69.0

TABLE III

Mole per cent. diphenyl	Initial cryst. temp., °C.	Final solidification temp., °C.
0.0	47.7	47.7
22.8	35.0	
30.7	30.3	24.9
37.2	25.9	
39.3 E	25.2	25.2
42.5	28.0	25.0
47.0	32.3	25.4
54.2	38.5	25.2
63.8	46.1	
78.0	56.2	
100.0	69.0	69.0

(II) **Diphenyl–Benzophenone.**—The freezing point–composition diagram for this system, constructed from the data given in Table III, is shown in Fig. 2.

This system also shows a simple eutectic. According to the intersection of the liquidus curves, the eutectic composition is 39.3 mole per cent. diphenyl and the eutectic temperature is 25.2°. A sample of this composition solidified at 25.2°. The average of the four final solidification temperatures in Table III is 25.1°. Using the method described under the previous system, we have shown that there is no appreciable solubility of the constituents in each other in the solid state. Assuming ideal solution behavior, we calculate that the eutectic composition should be 41.3 mole per cent. diphenyl and the eutectic temperature should be 23.5°. Here again, due to one constituent being polar and the other non-polar, solubilities are lower than ideal.

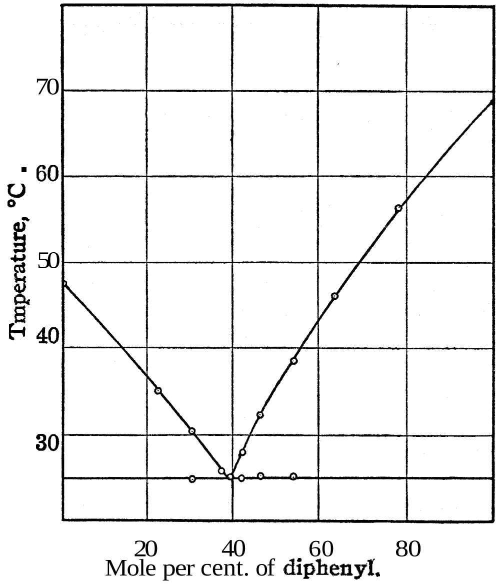

Fig. 2.—Diphenyl-benzophenone.

(III) **Benzophenone–Diphenylamine.**—The unbroken freezing point–composition curve in Fig. 3 is constructed from our data given in Table

IV and the broken curve from our data in Table V. The dots in the figure represent points reported by Giua and Cherchi.[2] The curve shows a compound with equimolecular quantities of diphenylamine and benzophenone and two eutectics; one at **30** mole per cent. benzophenone and at 34.1°; the other at 74.5 mole per cent. benzophenone and at **31.9'.** Due to the marked interaction between these polar compounds, solubilities are much higher than ideal. There is definite evidence that there are two forms of the compound. If a sample consisting of the compound composition is melted and then solidified in an ice–salt bath, crystals of the metastable compound are obtained. These crystals melt sharply at **30.8'.** When this melt is agitated, it solidifies completely, yielding crystals which melt sharply at 40.2°. Although the transition temperature has not been determined, it is definitely below room temperature. **A** sample of the metastable solid

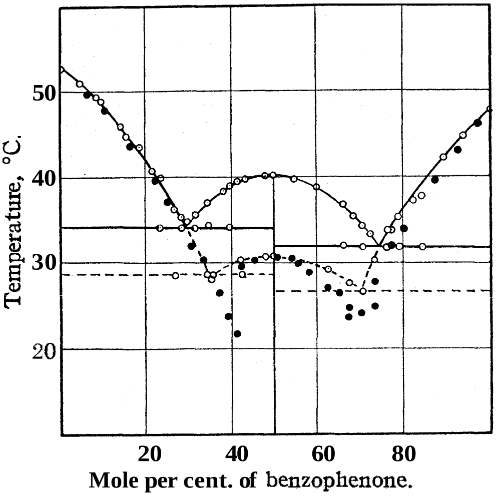

Fig. 3.—Benzophenone–diphenylamine.

TABLE IV

Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.	Disappearance of solid, °C.	Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.	Disappearance of solid, °C.
0.0	52.8	52.8		48.2			40.1
4.7			51.0	50.0 Compd.			40.2
8.5	49.3			54.5	39.7		40.0
9.3			49.0	60.0			38.7
14.0			46.0	66.5		32.2	37.0
15.5	44.8			68.4			35.4
18.8			43.5	70.5	34.5	31.8	34.4
21.7	40.8			72.2			33.5
23.5	38.9	34.1	40.0	74.5 E		31.9	
27.0	36.3			76.2	34.0	31.8	34.1
28.5	35.5	34.1	35.0	77.6	34.0		
30.0 E	34.1	34.1		79.0	35.4	32.0	35.5
31.7		34.1	35.6	82.4	37.3		
34.8		34.3	37.2	84.1	37.6	31.7	37.5
38.2			38.3	89.4	42.1		42.4
39.8		34.2	39.1	94.7			45.0
41.2			39.5	100.0	47.7	47.7	
43.2			39.7				

TABLE V

METASTABLE COMPOUND

Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.
27.0	36.3	28.6
34.8 E'	28.6	28.6
35.8		28.6
42.6	30.5	28.6
48.2	30.8	
50.0 (M.S. **Compd.)**	30.88	30.88
62.8	29.4	
67.8	27.8	
70.5 E′(?)		26.6
73.6	30.2	

compound was largely converted into stable solid in fifteen hours at room temperature.

In general, on cooling melts containing from **31** to **74** mole per cent. of benzophenone, initial crystallization temperatures which fall on the metastable curve will be obtained unless the samples are carefully inoculated with crystals of the stable compound. Due to the marked tendency of the compound and of benzophenone to undercool, most of the points on the unbroken curve (Fig. **3)** were obtained by thermostating samples for eight to twelve hours to determine the temperature at which the last of the solid phase disappeared. However, a number of points were checked by carefully determining the temperature of initial and final crystallization.

Up to **30** mole per cent. and in the range above **75** mole per cent. benzophenone, the data reported by Giua and Cherchi, based entirely on cooling curves, are in fair agreement with ours. In the region **30** to **75** mole per cent. benzophenone, their curve is somewhat similar to our metastable curve, but most of their points are too low, evidently due to undercooling. It is very difficult to obtain reliable data in the vicinity of the eutectic between metastable compound and benzophenone. This eutectic temperature may be in error by as much as **2** or 3°.

Summary

1. The freezing point–composition diagram for the system diphenyl–diphenylamine shows a simple eutectic at **41.7** mole per cent. diphenyl. The eutectic temperature is **29.5'.**

2. In the diphenyl–benzophenone system, there is likewise a simple eutectic at **39.3** mole per cent. diphenyl with a eutectic temperature of 25.2°.

3. Diphenylamine forms an equimolecular compound with benzophenone. The stable compound has a melting point of **40.2'.** The eutectic between compound and diphenylamine occurs at **30.0** mole per cent. benzophenone and at **34.1'.** The eutectic between compound and benzophenone occurs at 74.5 mole per cent. benzophenone and at 31.9'. Evidence is presented for the existence of a metastable form of the compound with a melting point of 30.8°.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 329]

The Kinetics of the Thermal Decomposition of Trichloromethyl Chloroformate

BY H. C. RAMSPERGER AND G. WADDINGTON

Trichloromethyl chloroformate gas is known to decompose at 300° to give two molecules of phosgene[1] as shown by the equation

$$ClCOOCCl_3 = 2COCl_2 \qquad (1)$$

The liquid can be decomposed at room temperature by the addition of various metallic chlorides such as aluminum chloride,[1,2] in which case, however, the reaction is

$$ClCOOCCl_3 = CO_2 + CCl_4 \qquad (2)$$

The rate of the thermal decomposition in the gas phase has been studied by us between 260 and 310° and in the pressure range 4 to 17 mm. with the intention of providing further data on unimolecular reactions.

Preparation of the Compound.—The method of preparation was similar to that of other investigators,[1,2] namely, the photochemical chlorination of methyl formate. A 100-cc. portion of methyl formate was placed in an all-glass apparatus provided with a reflux condenser cooled with ice and salt to prevent loss of the very volatile methyl formate. The flask containing the methyl formate was illuminated by a 500-watt lamp placed just above it. To avoid explosions illumination was commenced before the slow stream of "tank" chlorine was passed in. The temperature was kept at about 30° during the initial stages of the reaction. As the chlorination progressed the chlorine was passed in more rapidly and the temperature was gradually increased until finally it reached about 90°. Chlorination was complete after thirty hours.

A portion of the product was distilled under reduced pressure in a small all-glass apparatus provided with a fractionating column and condenser. The middle fraction of a sample, which boiled between 50.0 and 50.1° under 48 mm. pressure, was collected in a bulb containing calcium chloride. This supply was frozen with a carbon dioxide–ether mixture, sealed onto a high-vacuum line, pumped off and allowed to diffuse over into a second bulb immersed in carbon dioxide–ether, after which the original container was sealed off. The sample (A in Fig. 1) could be partially evaporated into the 500-cc. bulb B, frozen back into A and any non-condensed gas pumped off. Repetition of this process ensured the elimination of dissolved gas.

Apparatus and Experimental Method.—A diagram of the apparatus is shown in Fig. 1. C_1, C_2 and C_3 are stopcocks specially designed to handle corrosive gases; these

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[1] Hentschel, *J. prakt. Chem.*, [2] 36, 99, 209, 305, 468 (1887).

[2] Grignard, Rivat and Urbain, *Ann. chim.*, 9 [13], 229 (1920).

have been described in detail elsewhere.[3] D is a mercury boiler, and E the reaction cell, which was heated to the desired temperature by boiling the mercury under a constant pressure, maintained by having a twenty-liter bottle connected with the system and adjusting by hand the small pressure changes due to changes in the room temperature. The cell was sealed to the boiler at F with a cement of litharge and glycerin and this was coated with sealing wax. This joint was cooled by a copper coil carrying a stream of water. This arrangement permitted the cell to be replaced easily by another cell and made it possible to use cells of various kinds of glass. The cells had a volume of about 125 cc., and the external volume in the tubing, stopcock and click gage was about 1.5 cc. No corrections were made for this small outside volume in the calculation of rate constants.

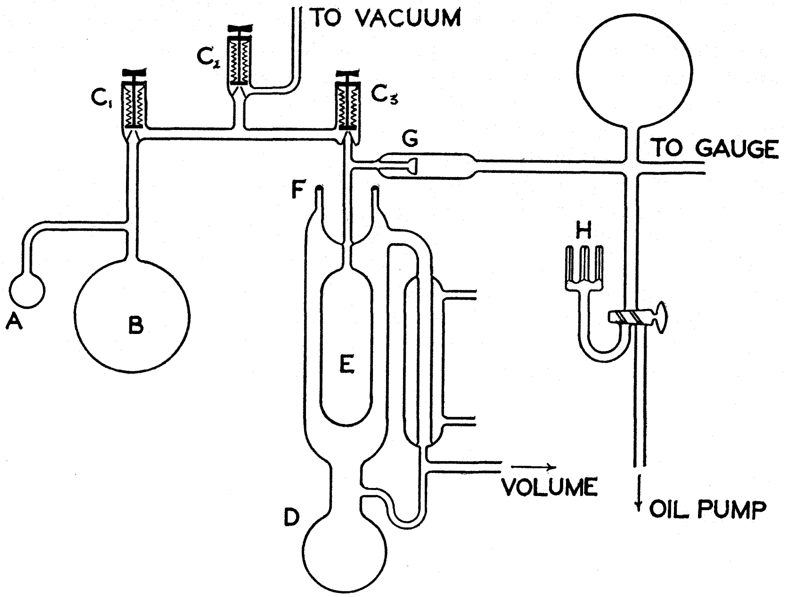

Fig. 1.—Apparatus.

Pressures were measured by means of the click gage G,[4] which was operated by admitting air through the controlled leak H until the click was heard. The pressure in the click system was then measured by means of a McLeod gage designed so as to measure accurately pressures of from 1 to 5 cm. In filling the cell the opening and closing of the stopcock C_3 required only a few seconds. Time measurements were started on closing C_3. Pressure measurements were then made at time intervals chosen so that the pressure increments were approximately equal, and were continued until the reaction was about 80% complete. The final pressures were obtained by allowing the reaction to go to completion; in the runs at lower temperatures time was saved by completing the reaction at a higher temperature and using the gas laws to calculate the final pressure at the lower temperature, it having been shown that the gas laws were obeyed by the reaction products.

Chemical Nature of the Reaction.—According to both equations (1) and (2) the final pressure should be exactly twice the initial pressure. This was verified by admit-

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[3] Ramsperger, Rev. Sci. Instruments, 2,738 (1931).

[4] Smith and Taylor, THIS JOURNAL, **46**,1343 (1924).

ting the compound to the cell and measuring its pressure at a low temperature where decomposition was negligibly slow. The temperature was then raised and the reaction carried to completion. The gas laws had been shown to be obeyed by the compound at lower temperatures. In this manner the final-to-initial pressure ratio was found in three experiments to be 1.99, 2.00 and 1.986. To distinguish between reactions (1) and (2) the reaction products, at about 3 cm. pressure, were frozen out in a side-tube with a carbon dioxide–acetone mixture at −79 to −80° The pressures from three experiments were 5.4, 5.6 and 5.0 mm., agreeing quite well with the vapor pressure of phosgene at this temperature, which is about 6 mm., and indicating that there could be no appreciable amount of carbon dioxide, carbon monoxide or chlorine formed. Freezing out with liquid air gave zero pressure in one case and about 0.05 mm. in another experiment, indicating the absence of non-condensable gases such as carbon monoxide. A direct analysis of the reaction product by hydrolyzing with excess standard sodium hydroxide and back-titrating with standard hydrochloric acid using methyl orange indicator gave 98% of the amount of acid required if the product were pure phosgene. Incomplete hydrolysis may account for the slight discrepancy. The evidence is thus quite strong that phosgene is the only product formed.

From the known free energy of formation of phosgene from carbon monoxide and chlorine,[5] it is found at 290° and a partial pressure of 1 cm. of phosgene that phosgene would be about 30% dissociated at equilibrium. It is also known that the rate of decomposition of phosgene at the above temperature is negligible.' Our experiments show definitely that only phosgene is formed; this would suggest that the rupture of the trichloromethyl chloroformate molecule gives two molecules of phosgene as the immediate products. Pure phosgene could not be produced from carbon monoxide and chlorine formed initially and subsequently recombining, for then the equilibrium between phosgene, carbon monoxide and chlorine would be produced.

Experimental Results

First order rate constants were calculated by the interval method using the equation

$$k_1 = \frac{2.303}{t_2 - t_1} \log_{10} \frac{P_{t_1}}{P_{t_2}}$$

where P_{t_1} and P_{t_2} are the partial pressures of trichloromethyl chloroformate at times t_1 and t_2 in seconds. Approximately equal amounts of reaction occurred during these time intervals. We have averaged these interval constants to obtain a rate constant for the run. No more refined statistical procedure used in obtaining an average constant would have made any material difference because of the exceptionally good first order rate constants obtained during the course of each run.

Since it was not possible to obtain a pressure reading until at least one-half minute after the beginning of a run, it was more accurate to calculate the partial pressure from the final pressure, using a factor of exactly two for the final–initial pressure ratio, this being justified by the experiments previously referred to.

Table I gives the complete data for three runs. The first column of figures refers to total observed pressures while the second column gives the partial pressures of trichloromethyl chloroformate.

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[5] Bodenstein and Plaut, Z. *phys. Chem.*, 110,399 (1924).

TABLE I

COMPLETE DATA OF THREE EXPERIMENTS

Experiment 2. T = 290.0°C. P_1 = 1.576 cm.

P, cm.	P_t	1, sec.	$k \times 10^3$ (sec.$^{-1}$)
1.576	1.576	0	
1.712	1.436	63	
1.888	1.260	181	1.11
2.087	1.061	334	1.12
2.279	0.869	513	1.11
2.484	.664	760	1.09
2.708	.440	1164	1.10
3.152	.000		

Experiment 5. T = 280°C. P_0 = 1.503

P, cm.	P_t	1, sec.	$k \times 10^3$ (sec.$^{-1}$)
1.503	1.503	0	
1.548	1.458	51	
1.674	1.331	206	0.588
1.857	1.148	454	.597
2.033	0.972	751	.558
2.227	.779	1132	.582
2.398	.607	1575	.561
2.589	.417	2215	.587
3.006	.000		

Experiment 9. T = 305.0°C. P_0 = 1.333

P, cm.	P_t	1, sec.	$k \times 10^3$ (sec.$^{-1}$)
1.333	1.333	0	
1.509	1.157	50	
1.886	0.779	188	2.87
2.129	.536	320	2.83
2.273	.392	432	2.79
2.423	.242	596	2.94
2.666	.000		

When no change in the nature of the cell was made or no extra surface was added, the average rate constant was exceptionally reproducible. It was found early in the research that there was some effect of the cell wall on the rate. This is best illustrated by Fig. 2, in which log k is plotted against $1/T$ for two series of runs. Series A was made in a Pyrex cell containing Pyrex tubing, the cell and contents having been treated with a chromic acid cleaning solution, while Series B was carried out in an empty Pyrex cell which had merely been wiped free of dust and flamed very thoroughly.

The curvature exhibited by the plot of Series A runs indicates that in these runs there were two simultaneous reactions differing in energy of activation, while the straight line of Series B shows that the reaction was homogeneous or very nearly so. All Series B runs, particularly those at lower temperatures, have lower rates than those of Series A. The results of Series A are typical of reactions in which in addition to a homogeneous reaction there is present a heterogeneous reaction of lower energy of activation. In Series B the heterogeneous reaction has been practically eliminated. When, however, the surface-to-volume ratio was increased tenfold by adding, to the cell used in Series B, Pyrex tubing which had been wiped clean and flamed, there was an increase of 15 or 20% in the rate at 290". If we assume that the original surface had the same catalytic activity as the added surface, then the wall reaction in Series B runs would amount to only about 2%. This fact, together with the straight line obtained in Fig. 2, is good evidence that these runs are practically homogeneous.

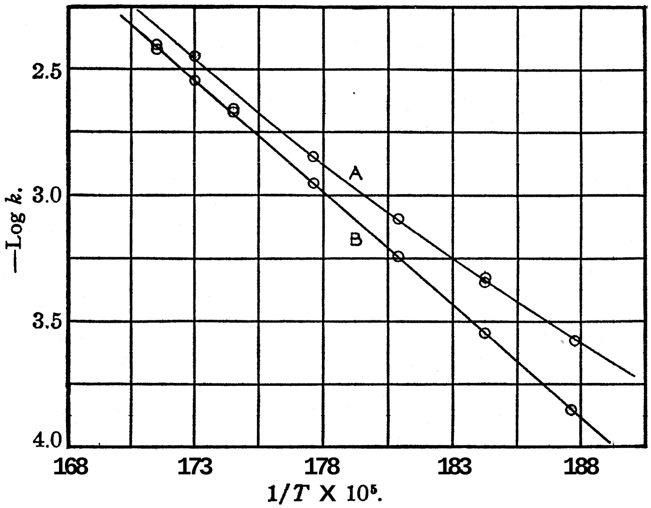

Fig. 2.—Curve A, cell packed with Pyrex tubing; Curve B, cell empty.

Many further unsuccessful attempts, using cells packed with tubing, were made to obtain surfaces free from catalytic activity. More careful flaming of the tubing sometimes gave results similar to those just described but in other cases the rates were faster. Various chemical treatments, such as thorough washing with cleaning solution, hot nitric acid or sodium hydroxide solution, again gave results similar to Series **A.** Treating the cell with hot concentrated hydrochloric acid often gave results which were identical with those of Series B, but with added tubing similarly treated the rates were again 15 to 20% faster. Soft glass or quartz cells gave rates which were 10 to 20% faster than Series B runs, The use of different samples of trichloromethyl chloroformate never altered the rate which had been characteristic of the cell used.

From the slope of the straight line of Fig. 2 the energy of activation is found to be 41,500 cal. per mole. The equation for the rate constant is $k_1 = 1.4 \times 10^{13} \times e^{-41,500/RT}$

Table II gives a summary of Series B runs.

TABLE II

Expt.	Temp., °C.	Initial pressure	Av. $k \times 10^3$	Number of constants	Expt.	Temp., °C.	Initial pressure	Av. $k \times 10^3$	Number of constants
11	260	1.640	0.143	6	9	305	1.333	2.86	4
4	270	1.293	.289	7	10	310	1.564	3.78	3
5	280	1.503	.579	6	12	310	1.472	3.98	3
2	290	1.576	1.11	5					
6	290	0.445	1.08	5	21	270	1.468	0.286	6
3	290	1.609	1.11	5	17	280	1.677	0.593	7
7	300	1.187	2.20	4	19	290	1.594	1.12	5
8	300	1.267	2.15	4	22	290	1.330	1.11	6
13	300	1.513	2.22	4	18	305	1.568	2.98	4
14	300	1.337	2.16	5	20	305	1.413	2.88	4
1	305	1.398	2.84	3					

The average of the average deviations of the rate constants for all runs is only 2.18%. Runs 17 to 22 were made with a new portion of the compound and reproduced the earlier experiments almost perfectly.

The first order constant is evidently independent of the initial pressure over the pressure range investigated. It would have been desirable to obtain data at lower pressures in order to test rather severely the theory of unimolecular reactions, but the catalytic effect of the walls at lower pressures would very probably be greater and would therefore be a serious disturbing factor.

We may calculate a lower limit to the number of oscillators required to agree with theory. An examination of specific heat data at high temperatures of highly chlorinated organic molecules such as carbon tetrachloride shows that these have unusually high specific heats. This would indicate that the oscillators of such molecules are of sufficiently low frequency that we will be justified in considering them as classical oscillators. Doing so, making use of the formulation of the calculation given by Kassel,[6] we then find that with the reasonable assumptions of fourteen oscillators and a diameter of 8×10^{-8} cm., the rate constant at 4 mm. pressure would be about 4% below the high pressure rate. Since the maximum number of oscillators which this molecule could contain is 18, we have here a reaction whose rate at the lowest pressures approaches fairly close to the maximum permitted by theory.

Summary

The thermal decomposition of trichloromethyl chloroformate has been studied over a temperature range of 260 to 310° and a pressure range from 4 to 17 mm. The reaction has been found to be first order and homogeneous save for a slight trace of wall catalysis. The rate constant is given by the expression

$$k_1 = 1.4 \times 10^{13} e^{-14,500/RT}$$

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[6] Kassel, "Kinetics of Homogeneous Gas Reactions." The Chemical Catalog Co., New York, 1931, p. 103, eq. 24.

The maintenance of the high pressure rate over the pressure range studied can be theoretically accounted for if the molecule is assumed to have a diameter of 8×10^{-8} cm. and to contain 14 classical oscillators.

The possible equilibrium between phosgene, carbon monoxide and chlorine was not found to occur as a result of the reaction, the sole product of the decomposition being phosgene.

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

The Effect of Gaseous Impurities on the Radiochemical Combination of Carbon Monoxide and Oxygen

BY CHARLES ROSENBLUM

Part of the recent work on the carbon monoxide oxidation under the influence of radon[1] involved a study of the effect of certain gaseous impurities possibly occurring in traces in the reactants as a result of the methods employed for their preparation. These foreign substances were water vapor, formic acid vapor and gaseous nitrogen.

The formic acid was prepared by reduced pressure distillation[2] in the presence of phosphorus pentoxide, and saturation of a $2CO{:}1O_2$ mixture was effected at 21.3°. Another sample of the reaction mixture was saturated with water vapor at 21.5°. A measured volume of tank nitrogen, purified by passing through a train containing, besides a liquid air trap, tubes of fused potassium hydroxide, sublimed phosphorus pentoxide and yellow phosphorus, was added to a third quantity of reactants. The gas mixtures so prepared were confined with radon in small spherical vessels[3] and the progress of the reaction followed manometrically.

Table I shows the reaction in gases wet with water vapor. Here $e^{-\lambda t}$ is the fraction of radon left after time t, E_0 is the initial amount of radon in curies, $P_{2CO + 1O_2}$ is the partial pressure of dry reactants, D is the diameter of the reaction vessel, and $(k\mu/\lambda)''_{\text{corr.}}$ is the velocity constant corrected for the catalytic efficiency of carbon dioxide and for the effect of recoil atoms.[1]

From the inverse square of diameter law[4] the velocity constant in a sphere of this size should be about 31,[1] which may be considered in agreement for experiments of this kind. It then appears that water vapor has little effect on the radiochemical carbon monoxide oxidation. That water vapor has a negligible effect is in accord with its radiochemically inert nature.[5]

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[1] Lind and Rosenblum, *Proc. Nat. Acad. Sciences*, 18, 374 (1932).

[2] Jones, *J. Soc. Chem. Ind.*, 38, 362T (1919).

[3] Lind and Bardwell, THIS JOURNAL, 47, 2675 (1925).

[4] Lind, *ibid.*, 41, 531 (1919).

[5] Duane and Scheuer, *Le Radium*, 10, 33 (1913).

TABLE I

THE INFLUENCE OF WATER VAPOR

D = 1.958 cm.; E_0 = 0.0451 **curie radon**

$e^{-\lambda t}$	$P_{2CO + 1O_2}$, mm.	$(k\mu/\lambda)''_{corr.}$
1.0000	740.1	
0.9705	700.2	34.0
.9277	647.5	32.6
.8869	602.2	31.2
.8479	564.6	28.6
.8106	530.5	28.5
.7691	492.7	30.0
.7243	456.6	28 0
.6771	423.0	26.2
.6329	393.0	26.3
.5872	363.4	26.5
.5387	334.0	26.2
.4923	308.8	24.8
.3787	255.1	24.0
.3358	235.2	25.1
.2933	218.7	23.0
.2507	202.0	23.7
.2042	183.7	24.5
.1532	159.4	31.5
.0606	122.1	28.4
	Av.	27.5

TABLE II

THE EFFECT OF FORMIC ACID VAPOR

D = 1.795 cm.; E_0 = 0.0425 **curie radon**

$e^{-\lambda t}$	$P_{2CO + 1O_2}$, mm.	$(k\mu/\lambda)''_{corr}$ I	$(k\mu/\lambda)''_{corr}$ II
1.0000	711.3		
0.9560	686.1	15.7	80.7
.9105	631.8	343	38.7
.8672	585.7	32.6	37.0
.8278	549.9	29.2	33.9
7911	517.3	30.1	34.7
7509	483.0	30.2	35.5
.6977	438.3	31.7	37.3
.6497	402.1	30.5	36.3
.5890	359.1	30.8	37.4
.5273	315.9	33.0	40.6
.4671	285.3	25.8	32.4
.4026	247.9	31.9	39.2
.3435	216.1	32.0	40.7
.2882	189.3	31.3	42.8
.1992	145.3	35.3	49.0
.1152	102.3	42.3	63.3

The effect of formic acid vapor is given in Table II.

The corrected velocity constants in column I are calculated in the usual manner directly from the pressure of reactants as indicated by the total pressure drop. The low constant for the first interval shows that **formic** acid is being decomposed, the formation of its decomposition products producing a pressure increase which masks the disappearance of carbon monoxide and oxygen.

It is impossible to say for certain what these decomposition products may be. The simplest assumption is either hydrogen and carbon dioxide or water vapor and the monoxide. However, supposing the formic acid to yield twice its volume in decomposition products, the partial pressure of reactants will be considerably less than was calculated simply from the total pressure drop. The result of this recalculation, confining the entire side reaction to the first interval, is shown in column II. These constants are somewhat higher than the expected value of **37.** However, it is apparent that the sole effect of formic acid vapor is to mask the main reaction in its earlier stages, and this only when present in appreciable quantities.

The effect of nitrogen was interesting in that it is an excellent ionic catalyst[6] as contrasted with the inefficient carbon dioxide. Furthermore,

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[6] **Lind and Bardwell, THIS JOURNAL,** 48, 1575 (1926).

this system involved the simultaneous effect of two radiochemical catalysts, a situation hitherto found only in the case of catalysis of the carbon monoxide oxidation by the relatively inefficient argon. In the following experiment, a mixture containing 33.8% nitrogen was used.

TABLE III

THE EFFECT OF NITROGEN

D = 2.006 cm.; E_1 = 0.0342 curie radon

$e^{-\lambda t}$	P_{2CO+1O_2}, mm.	$(k\mu/\lambda)'_c$	$(k\mu/\lambda)'_{corr.}$		$(k\mu/\lambda)''_{corr.}$	
		I	II	III	IV	V
1.0000	727.1					
0.9705	662.3	92.4	78.6	52.7	51.0	41.0
.9394	591.6	106.0	88.9	57.7	61.2	40.9
.9105	535.2	101.3	83.4	52.5	40.7	42.0
.8803	477.9	109.6	88.4	53.8	51.9	41.1
.8511	426.9	112.9	88.9	52.3	50.3	39.3
.8136	365.0	122.0	93.3	52.4	50.3	38.8
.7658	299.0	121.9	88.2	46.7	44.7	34.4
.7321	254.3	140.3	99.0	49.2	46.9	34.6
.6925	207.0	151.8	99.6	46.4	44.1	32.6
.6436	154.7	174.0	103.6	46.4	44.0	31.9

Inspection of velocity constants indicates unmistakably the efficient nature of nitrogen as an ionic catalyst. Column I shows the velocity constant $(k\mu/\lambda)'_c$ calculated from total pressure drop disregarding ionization on the catalysts. Column II corrects for the catalytic effect of carbon dioxide, assuming its efficiency to be 14.5%.[1] Attributing in addition 100% efficiency as a catalyst to the nitrogen, column III is obtained. Making proper correction for the effect of recoil atoms column IV is calculated from column III.

Since the corrected constants $(k\mu/\lambda)''_{corr.}$ should be about **31,** we are evidently faced with a significant velocity increase. The simplest manner of accounting for this increase is to assume an enhanced efficiency of the ionization falling on the carbon dioxide when in the presence of such an efficient catalyst as nitrogen. Assuming an efficiency of 30% for carbon dioxide, column V is obtained, which is a decided approach toward a correct representation of the reaction velocity.

A mechanism for such an unexpected effect cannot be suggested because the bulk of the sensitized radiochemical effects studied have involved only single catalysts. The result in the case here reported seems to indicate transfer of ionization by the efficient catalyst (nitrogen) not only to reactants but as well to the less efficient catalyst (carbon dioxide).

Summary

The effect of water vapor, formic acid vapor and nitrogen on the combination of carbon monoxide and oxygen in the presence of radon was studied. Water vapor had a small retarding effect on the reaction. For-

mic acid vapor did not directly affect the velocity of the main reaction, tending only to mask its course in the early stages by undergoing decomposition. Nitrogen had an extreme accelerating influence on the oxidation, which could be explained by an increase in the catalytic efficiency of carbon dioxide from 14.5 to 30%, in addition to the 100% efficiency of nitrogen.

MINNEAPOLIS, MINNESOTA
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR HARVARD UNIVERSITY]

An Anomalous Decomposition of Ozone in the Presence of Chlorine

BY LAWRENCE J. HEIDT, GEORGE B. KISTIAKOWSKY AND GEORGE S. FORBES

Several investigators[1] of the decomposition of ozone in the presence of chlorine have reported that the quantum yield, ϕ (ozone molecules decomposed per quantum absorbed), is 2.0 ± 0.2 in spectral regions where chlorine only absorbs, that the light reaction is nearly independent of the concentrations, and that the dark reaction[2] is relatively small at room temperature. The dark reaction has since been studied at 35 and 60° by Hamann and Schumacher.[3] The photolysis has been used as an actinometer.[4] The observations by Allmand and Spinks[1a] indicated that the course of the reaction was decidedly irregular. We undertook its further study at lower temperatures using an apparatus—ecently devised for referring ϕ in gas reactions to uranyl oxalate as an actinometer. Attention is called to the stringent precautions there described regarding temperature control and pressure measurement. A second paper of Allmand and Spinks[6] stated, as we had noticed in the meantime, that the dark reaction and wall effects were important, and expressed regret that these had not been further studied. None the less, they still viewed their reaction as essentially photochemical. These workers found that with O_3 greater than 35% and Cl_2 about 1%, values of ϕ up to 59 could be obtained; these values decreased as the light intensity, I, increased, the reaction rate being approximately proportional to I'"; the 10° temperature coefficient of the rate under these conditions was about 1.5, as compared with 1.0 when the chlorine percentage was higher, ϕ smaller, and the rate proportional to I.

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(1) For a review of the literature see (a) Allmand and Spinks, J. *Chcm. Soc.*, 1652 (1931); (b) Taylor, *J. Phys. Chcm.*, 34,2082 (1930); (c) Schumacher and Wagner, Z. *physik. Chem.*, [B] 5, 199 (1929); (d) Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co , New York, 1929, pp. 601–606; (e) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York 1932, pp. 254--262.

(2) Bodenstein, Padelt and Schumacher, Z. *physik. Chem.*, [B] 5, 209 (1929).

(3) Hamann and Schumacher, *ibid.*, [B] 17, 293 (1932).

(4) Cremer, *ibid.*, 128, 285 (1927).

(5) Forbes, Kistiakowsky and Heidt, THIS JOURNAL, 54, 3246 (1932).

(6) Allmand and Spinks, J. *Chcm. Soc.*, 599 (1932).

When high initial values of ϕ were obtained, they decreased rapidly; a similar sort of decrease is noted, under different conditions, in the present paper.

The quantum yield apparatus (Ref. 5, Fig. 2) was fused to the Pyrex train for introduction of ozone and chlorine at **A** (Fig. **1** of the present paper). Originally, the latter lacked the U tubes, U_1 and U_2, and greased stopcocks were present at F, G, H, I and J. The average quantum yields, ϕ, of thirteen preliminary experiments are noted upon the curves in Fig. 2.

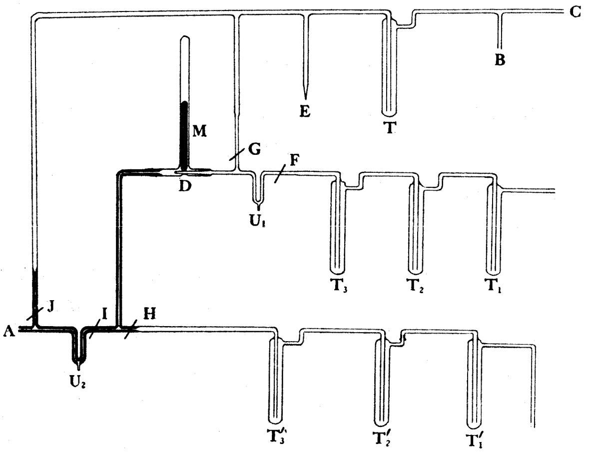


Fig. 1.

In all the figures black circles indicate darkness, open circles light absorption averaging 2.7 X 10^{15} **quanta/sec., λ = 366 mμ,** and half black circles exposure to red and yellow light. Plain circles indicate a temperature constant within **0.1°** at approximately **2°**, one flag **13°**, two flags **25°**. Whenever a new symbol appears, it defines conditions back as far as the last old symbol. Along a dotted line the temperature, θ, is indeterminate. To avoid implications regarding reaction mechanism we report only the rate of increase in total pressure, $dp/dt = m$, referred to **0°** in **mm.** of mercury per minute. Curves representing long experiments, e. **g.**, the fourth, are broken up into sections. When a part of the experiment between sections has been omitted, the total pressure, p, at the beginning of the section is noted. Initial partial pressures are given in the accompanying tables, with $p_f - p_i$, the difference between total final and total initial pressure.

The values of ϕ in Fig. 2 are not concordant, and are in most cases smaller than 2. The irregularities seem to be independent of partial pressures of reactants. The behavior of the mixture when light and dark periods alternated, shown in the group of curves to the left in Fig. 2, differs strikingly from that observed by **Allmand** and **Spinks**[1a] in that no periods of diminishing pressure occur. Our experiments did not become consistent when the rubber grease, R, in the stopcocks was replaced by a mixture of vaseline, V, with naphthalene, N, **refluxed** for many hours in an atmosphere of chlorine, or by concentrated sulfuric acid, S.

Suspecting contamination of the gases or of the cell, we improved the apparatus by adding U_1 and U_2, and by eliminating all stopcocks. All parts were heated in sulfuric plus nitric acid, washed with distilled water several times after washings had become neutral, and scrupulously dried. The quartz reaction cell (Ref. 5, Fig. 2) was pumped out for several hours with a Wagner deka-micro oil pump. Air, dried with resublimed phosphorus pentoxide, was then admitted. While fusing the parts together, we blew through a sodium hydroxide tower and a trap filled with glass wool and immersed in liquid air. At B, connection was made with a McLeod gage (not shown). A two-stage mercury diffusion pump backed up by the Wagner pump was connected to the train at C through the trap, T, immersed in liquid air to intercept mercury vapor. After testing for leaks with a Tesla coil, the train was pumped out with the diffusion pump, while flaming exposed parts. Dried air was admitted through E.

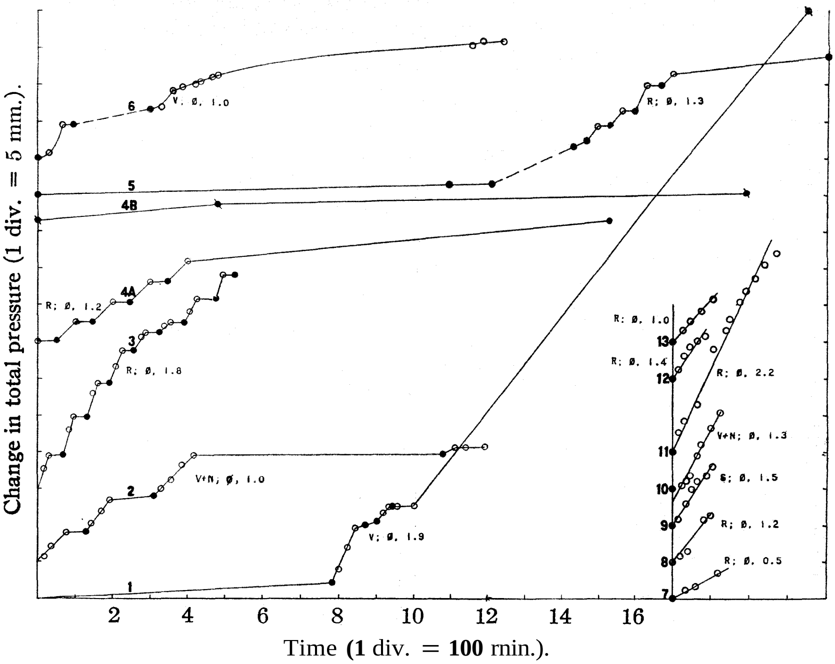


Fig. 2.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_t - P_i$
1	300	0	60	150
5	71	96	406	36
11	55	144	494	28
13	59	64	351	30

In dim diffused light tank chlorine was fractionally distilled in a vacuum three times, occupying successively traps T_1, T_2, T_3 and the graduated tube below U_1, previously calibrated by measuring the pressure developed in the reaction vessel, C_g, by evaporation of liquid chlorine between various graduations. The chlorine was evaporated each time at $-80°$ and the middle portion only was condensed in liquid air. Seals were made at F and G. Ozone was obtained from an apparatus lent by Professor E. P. Kohler. The electrolytic oxygen passed through sodium carbonate solution, solid potassium hydroxide, sulfuric acid and phosphorus pentoxide, in the order mentioned. The ozone was thrice fractionated much like the chlorine by suitable manipulations of a container of liquid air, the middle fractions occupying successively T'_1, T'_2, T'_3 and the calibrated tube below U_2. A seal was then made at H. Keeping U_1 and U_2 in liquid air, the sealed capillary at D was broken by the magnetic hammer. M, and a predetermined amount of chlorine distilled into the arm of U_2 next to D. Seals were made at I and J and allowed to cool. The total volume of U_2 and connecting capillaries to the left of I and J did not exceed 2 cc. or 5% of C_g. In experiments where much chlorine and little ozone was present in U_2, the liquid air could be removed at once from U_2 so that all the ozone passed into the cell for a pressure reading while the chlorine still remained solid. After the chlorine had evaporated, the pressure was read again. If little chlorine was present in U_2, the liquid air was manipulated so that the gases distilled over together into C_g; the chlorine could then be estimated only from its liquid volume. Exposed tubes connected with C, were wound with black tape.

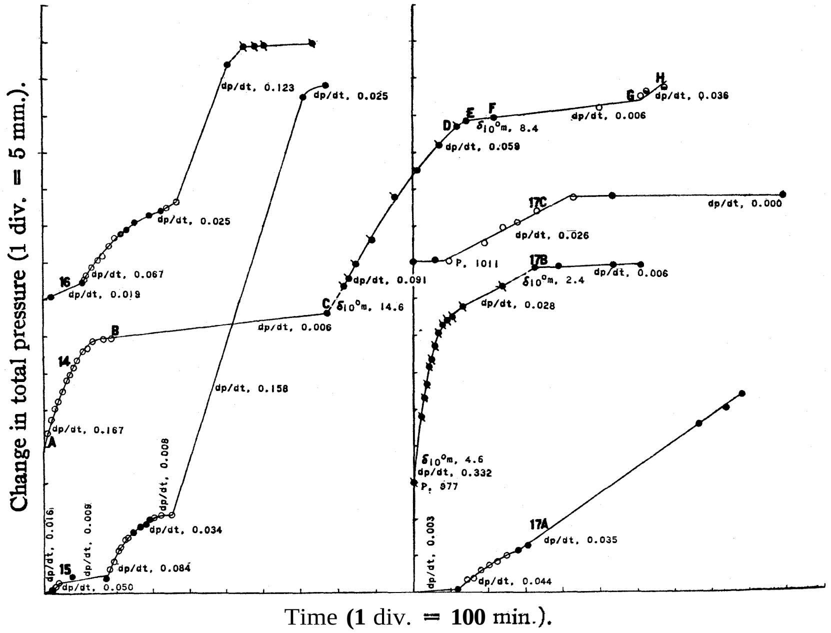


Fig. 3.

Expt.	PO,	Po,	p_{Cl_2}	PI—PI
14	147	140	374	74
15	135	133	170	68
16	132	97	300	66
17	158	130	651	79

For Experiment 14 the cell was on the diffusion pump for three hours at 25" before filling at 25°. At the start $\phi = 3$ at 2° decreasing toward B, where but a quarter of the ozone had been decomposed. The light was shut off at B. Between A and B the dark reaction was negligible. From B to C, $m = 0$ 006 and no further deceleration was observed. At C, θ was raised to 13° and the ten-degree temperature coefficient, $\delta_{10°}$ m, was 14.6, a highly abnormal value suggesting the emergence of a new type of reaction, possibly a chain reaction starting on the walls. Some deceleration occurs from C to D, presumably due to a decrease in p_{O_3}. At E, e again was lowered to 2° whereupon m from E to F was 0.006 in spite of a loss of three-quarters of the ozone remaining at C. From F to G ultraviolet light was without effect.. From G to H, red light through the exit slit produced acceleration. Beyond the last recorded reading, in this and all other experiments, residual ozone was decomposed by prolonged exposure to the full light of a

Uviarc, 3 cm. from the front window. Given the final reading of total pressure, all partial pressures corresponding to any given reading of total pressure could be calculated.

Before Experiments 15 and **16**, the cell was pumped out at 25° for one day with the oil pump and for a second day with the diffusion pump. Gases were introduced at 2" as in following experiments unless otherwise noted. The initial value of ϕ was 3. In each case a condition was soon attained where alternation of light and darkness had little effect upon the trend of the curves. The "fast" reaction began without elevation of temperature soon after the light was shut off. In 15, and to a considerable extent in **16**, the gases became insensitive to ultraviolet light just before the fast reaction set in. Ozone undecomposed at the end of the experiments amounted to **127** and **108** mm., respectively.

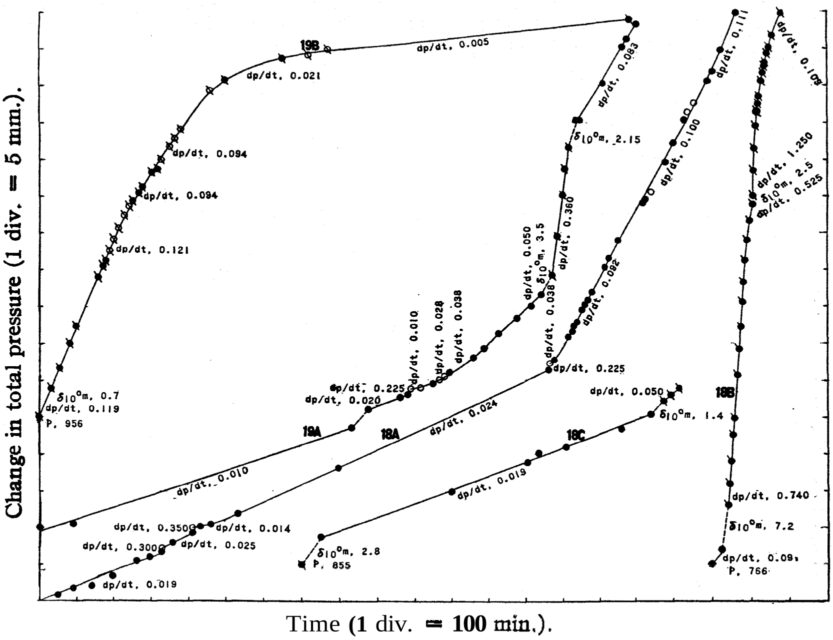


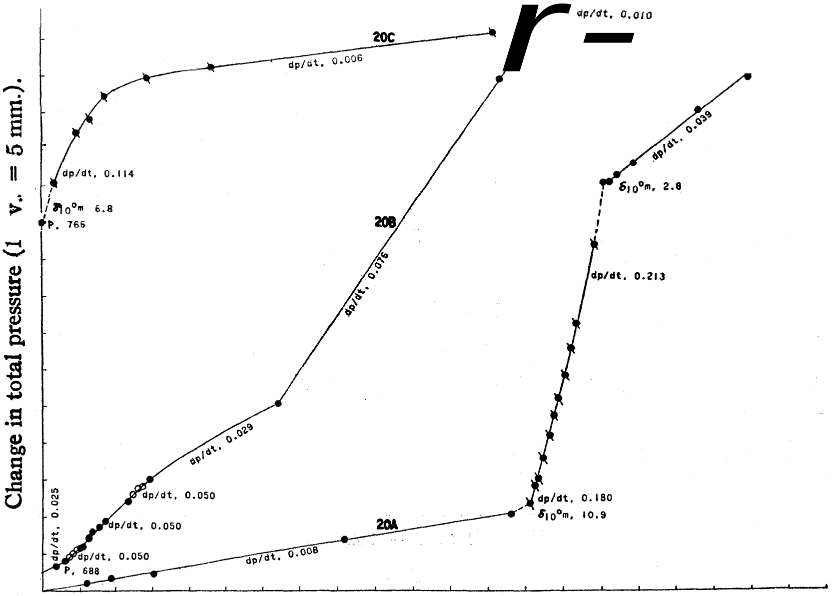
Fig. 4.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_t - p$
18	570	32	60	285
19	457	249	105	229

Figure **2** should now be reexamined. In Experiment **1** the cell was almost as clean as in 14, and little accumulation of impurities from stopcocks could have occurred; initial $m = 0.006$. The curve up to the intervention of the fast reaction, while somewhat terraced, is not very different from the curve in **14**. Subsequent experiments **2**, 3, 4, 5 and 6, between which the cell was pumped out but not otherwise cleaned, show a pronounced and persistently terraced pattern but no fast reaction occurs except possibly over a short interval in Experiment 6.

Before Experiment **17** the cell was removed from its copper thermostating jacket, cleaned as before **14** and pumped out with the oil pump while heated to dull redness. Dry air was then admitted. Although $\phi = 0.8$ (uncorrected for the dark reaction) was relatively small at the start, the slope attained after admission of light remained nearly unaltered in light and dark alike until θ was raised to 22°; δ_{10° m $= 4.6$ is again large. One is tempted to connect the practical absence of the terraced pattern in the curve after light admission with the fact that the walls were cleaner than in previous experiments. After cooling, the decomposition reverted nearly to the original dark rate, m = 0.006, as against 0.003 and the system had regained its sensitiveness to light. Residual ozone was 24 mm.

Experiments 18, 19 and **20** in Figs. 4 and 5 are characterized by high initial ozone pressures. They show the impossibility of predicting the time intervening or the amount of photochemical or thermal reaction occurring before the beginning of **a** fast reaction. Further, they show that the fast reaction may suddenly start at any one of the temperatures used and is not dependent on a change of temperature or illumination. They also show that the fast reaction may die down and later reappear and that the induction period preceding the inception of the fast reaction decreases as experiments **are** started at successively higher temperatures.



Time (1 div. = 100 **min.**).

Fig. 5.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
20	406	118	90	203

Since Allmand and Spinks[18] used a sulfuric acid manometer, Experiment **21** was carried out with **1** cc. of pure concentrated acid in the cell (wetting only a corner of C_g). The initial dark reaction at **2°** **was** about the same as in other experiments. Upon **warming** to 21°, $\delta_{10^\circ}\, m$ was 4.6, and upon cooling **to** 2° again, δ_{10° **m** was 11.8. Light now accelerated the reaction moderately and the terraced pattern persisted, the reaction rate promptly decreasing when light was shut off. Again we observed no periods of decreasing pressure, such as those described by **Allmand** and Spinks. In the presence of sulfuric acid only we observed at 2° a white mist, formed in many of their experiments also, and found by them to contain perchloric acid. Our mists slowly disappeared on raising the temperature to 25°.

Experiment **22,** a repetition of **21,** agreed throughout with **21** and need not be discussed in detail.

In Experiment 23 the cell walls were entirely covered with sulfuric acid, the excess being poured out. The photochemical behavior was essentially the same as in **21** and **22,** but δ_{10° **m** is smaller, indicating a further retardation of the fast reaction.

Before Experiment **24** the sulfuric acid was very carefully washed out, and **1 cc.** of water was introduced. After fusing the cell to the train, the cell was pumped and filled while a block of carbon dioxide ice was held in contact with the front window to prevent evaporation of the water. At the start, at 2°, $p_{O_3} = 369$. $p_{O_2} = 125$, $p_{Cl_2} = 300$ and $m = 0.004$. Warmed to 22°, δ_{10° m = **8.25,** after which m suddenly fell off with the cell still at 22°, to a quarter of its previous value. It then suddenly trebled, and was later cut in half. In the final stages of the experiment $\delta_{10^\circ} m$ was **3.5** and **0.9,** respectively, as the reaction progressed

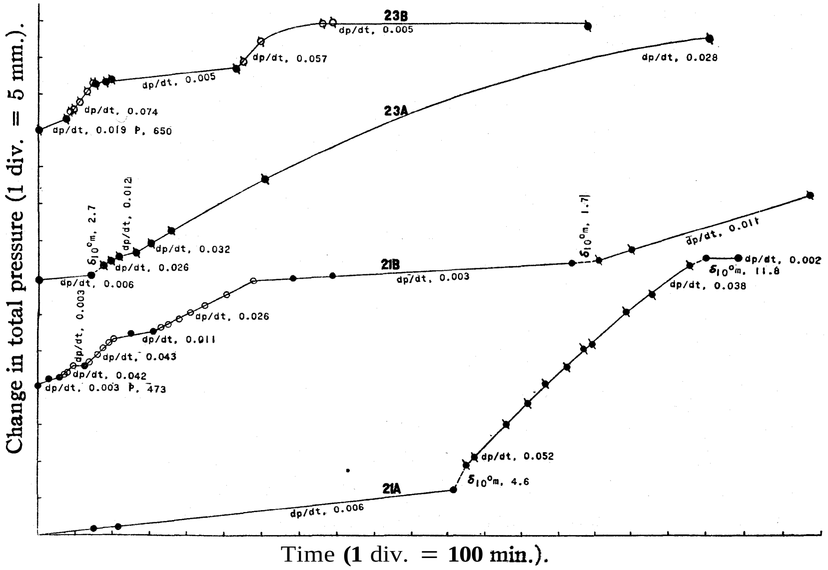


Fig. 6.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
21	194	54	185	97
23	157	356	80	79

Experiments **21** to **24** prove that variations in m (θ constant) are less striking **in** the presence of sulfuric acid or water, but persist even when the walls are completely covered with one of these liquids, that is, in the absence of an uncontaminated quartz surface. On the other hand, a mixture of ozone and chlorine does not become insensitive to light when the whole surface of the cell is contaminated.

In Experiment **25** ozone without chlorine was carefully investigated over two hundred hours to substantially complete decomposition, one hundred pressure readings being made. The cell had been scrupulously freed from add, flamed and pumped for a whole day. At the start, at **2°**, $p_{O_3} = 490$, $p = 623$ and $m = 1.20$. After two and one-half hours p was only **653,** but m had decreased to **0.026,** following a pseudo-logarithmic curve. Raised to 22°, m was not quite doubled. Exposed behind the slit to red light, m at once increased to **0.165** but fell off gradually without increase at any time to **0.012** for p = **795,** the corresponding dark rate being **0.002.** These results agree substantially with a previous investigation by one of us,[7] except for the initial rapid dark reaction above described. Kassel,[8] indeed, mentions the disagreement among previous workers in this respect. It might be urged that the fast reactions observed in the dark in the earlier stages of our experiments with chlorine present also depend upon the rapid decomposition of ozone per se, but the fast reactions springing up in the later stages of the experiments with chlorine find no counterpart upon the curve of pure ozone.

In Experiment **26** C_8 was replaced by a 50-CCPyrex bulb, very carefully cleaned, and flamed while the diffusion pump was running. The bulb was filled at 23° and the reaction studied only in the dark at 23, 35 and 50° with the usual precautions. From p_{O_3} = **518,** p_{Cl_2} = **70** and p = **652** to p = **705** at 23.2°, m changed from **0.476** to **0.435.** At **35.2"** for p = **740** to **760, m = 0.905** or $\delta_{10°}$ m, **1.74.** At **49.2"** and p = **790,** m = **2.32** decreasing to **1.17** at p = **835** or $\delta_{10°}$ **m = 1.84.** At **25.2"** and p = 843, m = **0.088** decreasing to **0.030** at p = **890** or $\delta_{10°}$ **m** = 5.55, At 35.2° and p = **892,** m = **0.073** decreasing to **0.037** at p = **894** or $\delta_{10°}$ **m** = **2.21.** At **49.5"** and p = **895,** m = **0.070** or $\delta_{10°}$ **m** = **1.35.**

The erratic values of $\delta_{10°}$ m indicate that the reaction is very complex in Pyrex as in quartz over a temperature range including that covered by Bodenstein and co-workers.[2,3] The results of these experiments do not lend themselves readily to a kinetic treatment. However, some general conclusions can be made. It is apparent that the more carefully the gases and the reaction system are purified, the more erratic are the results and the more pronounced is the fast reaction. Hamann and Schumacher[3] found some indications of this fast reaction with gases which perhaps were as pure as those used here. This undoubtedly constitutes an agreement between their work and ours. Experiments with sulfuric acid and water point rather against a pure wall reaction as the cause of phenomena here described. It seems instead more likely that an unstable intermediary product (Hamann and Schumacher suggest ClO) accumulates in the absence of impurities and causes a fast decomposition of ozone in a chain reaction which is sensitive to alterations in experimental conditions so minute that they were beyond our control. This last circumstance makes it unprofitable to discuss here the reaction mechanism in greater detail.

The fast reaction observed in our experiments is very probably analogous to the explosions of bromine–ozone mixtures reported by Lewis and Feitknecht.[9] The difference appears to be in degree only,[and attributable to the stability of chlorine oxides, greater than that of bromine oxides, which prevents the production of a real explosion.

Summary

The decomposition of ozone in the presence of chlorine has been reinvestigated at 2, 13 and 22° in quartz and in Pyrex at 23, 35 and 50° with

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[7] Kistiakowsky, *Z. physik.* Chcm., **117**, 337 (1925).

[8] Kassel, Ref. If, p. 264.

[9] Lewis and Feitknecht, THIS JOURNAL, **53**, 2910 (1931).

great care in pressure measurement, temperature control and avoidance of contaminations. Each gas was thrice fractionated, stopcocks were eliminated and the cell walls freed from adsorbed impurities. As such precautions became more stringent, the speed of the dark reaction following a brief exposure to light, an increase in temperature or even a period in the dark at 2, 13 or 23° tended to increase surprisingly. After this, an equally striking decrease often occurred.

The time intervening before inception of the fast reaction decreased with an increase in the temperature and was shortened by absorption of light by chlorine. Temperature coefficients became highly abnormal, ranging from 0.7 to 14.6. At the same time the quantum yield, corrected for the dark reaction, fell off from two or more to very small values. Reaction velocities and temperature coefficients sometimes became small again, after which the system tended to regain sensitiveness to light.

Concentrated sulfuric acid or water, within the cell, inhibited but did not eliminate these anomalies. They were at a minimum when greased stopcocks were used in the gas train.

Uncontaminated ozone, without chlorine, gave a fast dark reaction at the start which died down during the first two and one-half hours and could not be restored during the next seven days by light of any available wave length or by temperature changes.

The fact that light is readily capable of starting the "fast" reaction is evidence for the essential similarity, if not identity, of the mechanisms of light and dark reactions.

We have attempted to explain the above observations in terms of a heterogeneous or a homogeneous reaction chain or in terms of a combination of both. No mechanism so far considered by us, including those given in the literature, seems to fit all our experimental data. We, therefore, prefer for the present to reserve their discussion.

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The Formation of Sodium Thiosulfate from the Oxidation of Sodium Sulfides by Means of an Aromatic Nitro Compound

BY JESSE LUNT BULLOCK AND GEORGE SHANNON FORBES

The oxidation of sulfide with the subsequent formation of thiosulfate has been recorded as early as 1798 by Berthollet.[1] Since that time many investigators have contributed to knowledge in this field, among whom may be mentioned Gay-Lussac, Vauquelin, Thomas and Rule, Kiister and Heberlein, and most recently Pearson and Robinson.[2]

In the field of organic chemistry, especially in the case of aromatic nitro compounds, the use of sulfide ion as a reducing agent has had wide application. This phase of the subject has been studied by Zinin, Beilstein and Kurbatow, Lobry de Bruyn and Blanksma, Brand, Vesely, J. B. Cohen and Flürscheim.[3]

We have restricted our work to the oxidation of sulfide, hydrosulfide, and polysulfide ions by aromatic nitro compounds. We have obtained information concerning the formation of thiosulfate ion.

Previous workers in this field have used nitro compounds that were not appreciably soluble in aqueous solution and have employed higher temperatures and mixed solvents. By the use of sulfonated aromatic nitro compounds—in particular sodium m-nitrobenzenesulfonate-we were able to work in aqueous solutions of 0.1 M concentration and at room temperature. In this oxidation thiosulfate ion and sodium *m*-amidobenzenesulfonate are the only products formed—sulfite ion was not found in any of our oxidations, see page 236. This enabled us to study the course of the reaction, which is traditionally formulated as follows

$$RNO_2 + Na_2S_2 + H_2O = RNH_2 + Na_2S_2O_3$$

Purification of Materials.—The materials involved could all be obtained in a very pure state or could be purified easily. In the case of sodium hydroxide this was prepared from C. P. sticks made up to a saturated solution with water in a seasoned Pyrex flask. The impurities, chloride, carbonate, and silicate, which may be present settle out on standing quite completely but the small quantities which remained in solution were without effect on the reaction as was proved by a series of blank tests.

Sulfur was purified by recrystallization from carbon disulfide.

Hydrogen sulfide was prepared by heating *p*-toluidine and sulfur together at 200–220°.[4] The resulting gas which is very pure was washed through water to remove any entrained solid.

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(1) Berthollet, *Ann. Chim.*, *26*, 233 (1798).

(2) (a) Gay-Lussac, *ibid.*, 85, 199 (1813); (b) Vauquelin, *Ann. chim. phys.*, *6*, 5 (1817); (c) Thomas and Rule, J. *Chem. Soc.*, 111, 1063 (1917); (d) Kiister and Heberlein, Z. anorg. *allgem. Chem.*, 43, 53 (1905); (e) Pearson and Robinson, J. *Chem. Soc.*, 1473 (1930).

(3) Zinin, *J. prakt. Chem.*, *27*, 149 (1842); Beilstein and Kurbatow, *Ber.*, 11, 2056 (1878); Lobry de Bruyn and Blanksma, *Rec. trav. chim.*, 20, 115 (1901); Brand, J. *prakt. Chem.*, 74, 449 (1906); Vesely, *Rec. trav. chim.*, 44, 352 (1925); J. B. Cohen, *J. Chem. Soc.*, *87*, 1266 (1905); Flürscheim, J. *prakt. Chem.*, 71, 497 (1905).

(4) Heumann, "Anilinefarben," Vol. III, p. 368.

The nitrobenzenesulfonate was prepared from purified nitrobenzene and the resulting sodium salt recrystallized.

Analytical Methods.—The standard iodine titration was used throughout for the determination of sulfide and thiosulfate ion. In the latter case the sulfide was removed by addition of a freshly prepared suspension of cadmium carbonate. Pure iodine was used as a standard of reference. Weighing burets were employed except in a few instances where time was of more importance than accuracy. Polysulfide sulfur was determined by a method of Küster and Heberlein.[2]

The Synthesis of Sodium Sulfides.—A very complete résumé of the work in this field is found in the paper of Pearson and Robinson already mentioned. We investigated all methods recorded in the literature. For the preparation of monosulfide and polysulfide in aqueous solution the method detailed by Kuster and Heberlein was employed with slight variations. By its use with all precautions it was possible to prepare solutions which contained only traces of thiosulfate. In non-aqueous solvents the tetrasulfide was prepared by bringing sodium and sulfur together under boiling toluene. This method has been variously described[2e] but by use of excess sulfur and boiling for twelve hours we obtained the tetrasulfide in a pure state. Pentasulfide was prepared by the method of Hugot.[5]

Another synthesis of sulfide which we employed in this investigation was to heat sulfur in aqueous sodium hydroxide until complete solution was obtained. The resulting solution was then allowed to stand at room temperature for forty-eight hours to attain equilibrium. This solution while it contained large amounts of thiosulfate gave valuable information when oxidized as will be shown later.

Experimental

The first part of the work was to determine the course of the oxidation. As has already been stated only thiosulfate results from the oxidation of sulfide ion by means of an aromatic nitro compound. Further in the case of mononitro compounds only amine is formed. One of us had established this point. The system that we were to study would contain, then, only sulfide, thiosulfate, and hydroxyl ions together with amine and the nitro compound. These latter had no effect on the analytical methods.

In the preliminary work we employed the solution obtained by the use of sodium hydroxide and sulfur. This solution is in equilibrium when $OH^-/S_x^=$ is 2.4 and polysulfide $S/S_x^=$ is 3.4. The thiosulfate ion does not enter into the equilibrium but is always formed according to reaction (4) page 236.

The reactions were carried out in a liter round-bottomed flask provided with a mechanical agitator. The flask was swept free of air by means of nitrogen and the solution introduced. Temperature was maintained within 0.1° by immersion in a thermostat of the usual type. Samples were withdrawn by means of a pipet, added directly to weighing bottles which contained weighed quantities of standard iodine or cadmium carbonate suspension as the case might be and the weight of the sample determined. A slow stream of nitrogen was passed into the reaction flask throughout the experiment. Blanks in this apparatus showed no air oxidation during six hours.

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(5) Hugot, *Compt. rend.*, **128**, 338 (1899).

During the course of the investigation nearly a hundred oxidations were made. Table I shows results obtained from typical oxidations.

TABLE I

DISULFIDE OXIDIZED BY SODIUM NITROBENZENESULFONATE

Temp., 25.0°; concentration of oxidizing agent, 0.1 M; time in minutes; data, moles per 1000 g. of solution

Time	Total iodine	$S_2O_3^=$	$S^=$	Time	Total iodine	$S_2O_3^=$	$S^=$
	No. 52				**No.** 54		
0	0.2424	0.0000	0.1212	0	0.2037	0.0067	0.0986
15	.1048	.0293	.0377	15	.0990	.0326*	.0299
30	.0998	.0372	.0313	30	.0939	.0384*	.0245
45	.0945	.0453	.0256	45	.0976	.0427*	.0242
60	.0955	.0489	.0233	60	.0955	.0489*	.0226
	No. 51				**No.** 53		
0	0.2520	0.0000	0.1260	0	0.0980	0.0255	0.0420
15	.1129	.0288	.0420	15	.0976	.0175*	.0228
30	,1055	.0392	.0331	30	.0931	.0268*	.0219
45	.1071	.0456	.0307	45	.0940	.0333*	.0191
60	.1020	.0505	.0258	60	.0947	.0373*	.0171
	Composite						
0	0.2000	0.0000	0.1000				
1	.1637	.0074	.0781				
2	.1399	.0113	.0643				
3	.1326	.0146	.0590				
5	.1234	.0196	.0519				
7	.1205	.0222	.0492				
10	.1180	.0248	.0471				

*** Represents increase over amount initially present. No. 52 solvent molal sodium chloride. No. 54 0.15 molal sodium hydroxide. No. 51 sodium sulfate, ionic concentration equal to unity. No. 53 polysulfide from solution of sulfur in sodium hydroxide.**

It will be noted that in every case the sulfide concentration diminishes rapidly at first while the thiosulfate-ion concentration does not increase at a proportional rate. The color of the reaction mixture is intensified and frequently there is a definite precipitation of sulfur. If a test of an early stage of the oxidation which has been treated with cadmium carbonate to remove sulfide ions is titrated with standard acid it is found that there is a large increase in the hydroxyl-ion concentration which is equal to the loss of anions containing sulfur, $S_x^=$ and $S_2O_3^=$. This would indicate that thiosulfate is not a direct product of the reaction as the stoichiometric equation shows but that the first products of the reaction are hydroxyl ion and sulfur—this is established in a quantitative way on page 236 reaction (2a). The sulfur as it is formed is taken up by the sulfide ion to saturation. However, when the hydroxyl-ion concentration has increased to the value given on page 233 for the $OH'/S_x^=$ ratio then the thiosulfate formation progresses uniformly (Table I, No. 53). Further oxidation is then conditioned by the thiosulfate formation since by equation (4), page 236, two sulfide ions are regenerated for each thiosulfate ion formed.

The data set forth in Table I can be utilized to give evidence of what has been briefly outlined above. In the case of disulfide oxidations at 25° there is no appreciable precipitation of sulfur and so from these few data the complete condition of the system is easily calculated.

The equation

$$S_2^{=} + RNO_2 + H_2O = S_2O_3^{=} + RNH_2 \qquad (1)$$

it is shown is made up of several, the first of which may be written

$$3S^{=} + RNO_2 + 4H_2O = 6OH^- + 3S + RNH_2 \qquad (2)$$

and the second

$$S^- + xS = S^{=}_{x+1} \qquad (3)$$

The cases of monosulfide and hydrosulfide were next investigated and it was found in both cases that there was an induction period of about thirty minutes before any appreciable oxidation began. Since the reaction was autocatalytic in character we investigated the effect of each of the known products of the reaction, RNH_2, OH^-, $S_2O_3^{=}$ and polysulfide S.

Table II shows this effect during the first minute of the oxidation.

TABLE II

Polysulfide sulfur	Fraction oxidized	Polysulfide sulfur	Fraction oxidized
0.00	0.0007	1.00	0.0295
.25	.0098	1.20	.0285
.50	.0225	1.50	.0260
.75	.0262	2.00	.0220
.83	.0263	3.00	.0160
		Satd.	.0146

Oxidations of saturated polysulfide were carried out in neutral salt solution and a good velocity constant obtained, using the bimolecular formula for different concentrations of (a) the oxidizing agent and (b) the total sulfide ion, both in moles per 1000 g. of solution.

TABLE III

Time	Total iodine	$S_2O_3^{=}$	$S_x^{=}$	k^a
0	0.1621	0.0020	0.0801	..
15	.1230	.0195	.0517	0.308
30	.1030	.0266	.0382	.292
60	.0840	.0410	.0215	.308
90	.0750	.0485	.0132	.320
120	.0715	.0535	.0090	.318

$^a\; k = \dfrac{1}{t(a-b)} \ln \dfrac{a(b-x)}{b(a-x)}$

Using concentrations greater than 0.11 molal of either sulfide or nitro compound the reaction ran too fast to measure with the requisite accuracy.

According to reaction (2) there should be a definite P_H which would allow the oxidation to progress without favoring the formation of thiosulfate. This was found to be close to PH 8. By the use of a borax-boric acid buffer oxidations were carried out which contained only a small amount of thiosulfate ion. Substituting boric acid in reaction (2) we obtain

$$3S^{=} + 12H_3BO_3 + RNO_2 = 3B_4O_7^{=} + 3xS + 17H_2O + RNH_2 \qquad (2a)$$

In an oxidation using this buffer the sulfur was filtered, thoroughly washed and dried. It was then dissolved in carbon disulfide, filtered, the solvent evaporated and the sulfur dried and weighed: calcd., 3.65 g.; found, 3.62 g.

The Formation of Thiosulfate.—As has been shown the oxidation of sulfide ion leads to the formation of hydroxyl ion and free sulfur. The formation of thiosulfate ion then takes place by a subsequent reaction which may be written as

$$6OH^- + 12S = S_2O_3^{=} + 2S^{=} + 3H_2O \qquad (4)$$

With regard to the formation of sulfite ions which are sometimes considered as intermediate in the formation of thiosulfate, we have shown that when a buffer is used only hydroxyl ion and sulfur result. All investigators agree that from the reaction between hydroxyl ion and sulfur only thiosulfate and polysulfide ions result. But if it were assumed that without a buffer the oxidation were carried further and sulfite were formed, then our analyses would show it. For it is well known and we have checked the fact in our work that sulfite and sulfide ions do not react rapidly or completely in alkaline solution. The behavior of solutions containing sulfite and hydrosulfide ions has been studied extensively by Foerster and his coworkers.[6] Their work shows that only under conditions of very careful adjustment of hydrogen-ion concentration is sulfite ion ever completely converted into thiosulfate. We employed the same method of analysis to determine sulfite as did Foerster and were not able to obtain a positive test in a single case.

Reaction (4) takes place rather rapidly at elevated temperature even with ordinary rhombic sulfur but at 25° the reaction is slow unless the sulfur is in an "active" state—set free by an oxidation of sulfide or in some similar way. We spent much time trying to prepare "active" sulfur but without success.

If one treats a pentasulfide ion with an excess of hydroxyl ion some of the sulfur in the polysulfide is available for this reaction and the solution on analysis shows an increase in sulfide and thiosulfate. Such a solution which tested 4.15 polysulfide sulfur, 0.675 sulfide and 0.207 thiosulfate after dilution with an equal weight of water was diluted with an equal weight of 0.1 M hydroxide and allowed to stand for two days. It then gave on analysis 0.748 sulfide and 0.243 thiosulfate. The sulfide increase is 0.073, that for thiosulfate 0.036—almost exactly two to one as shown by

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(6) *Foerster, Z. anorg. allgem. Chem., 177, 61* (1928)

equation (4). This ratio holds for all temperatures. The value of the polysulfide sulfur/$S_x^=$ ratio is a function of the temperature, the hydroxyl-ion concentration and the ionic strength of the solution where neutral salt is employed.

In a series of experiments where neutral salt was employed—sodium sulfate in ionic strength equal to unity—together with hydroxyl ion of varying concentration, we obtained for variation of hydroxyl ion from 2.4–5.7, polysulfide sulfur 3.4–1.0 correspondingly. Kiister and Heberlein, in a paper already cited, obtained in pure monosulfide solution the value 4.24 for polysulfide sulfur.

The Use of Other Aromatic Nitro Compounds.—While the greater part of the work was carried out with m-nitrobenzenesulfonate we prepared a set of other nitro compounds and measured their oxidizing rate against the one just mentioned. These results are set forth in Table IV. The compounds were synthesized with great care and were recrystallized from aqueous solution and dried to constant weight as sodium salts.

TABLE IV

Name	Relative speed of oxidation of disulfide
1-Nitro-4-carboxybenzene	1.263
1-Nitro-3-sulfobenzene	1.000
1-Nitro-3,5-disulfobenzene	0.962
1-Nitro-5-sulfonaphthalene	.95 app.
1-Nitro-4-methyl-3-sulfobenzene	.935
1-Nitro-3-carboxybenzene	.918
1-Nitro-2-oxy-3-carboxy-5-sulfobenzene	.425
1-Nitro-2-methyl-5-sulfobenzene	.417
1-Nitro-8-sulfonaphthalene	.4 app.
1-Nitro-2-carboxybenzene	.089

The chloro derivatives were abnormal, giving very rapid oxidation analogous to dinitro compounds.

From the data in Table IV it is seen that the para substituted compound oxidizes most rapidly. The meta substituted compounds all react at about the same rate while the ortho substituted compounds have very little oxidizing power.

The Effect of Temperature.—While reduced temperature slows down the rate of oxidation—reaction (2)—the effect is much more pronounced in thiosulfate formation—reaction (4). Below 25° the solution of sulfur is so slow that the greater part of it is precipitated in an unreactive form even in excess of hydroxyl ions. Thus the oxidizing power of sulfide ion is diminished, for it will be noted by reference to reaction (4) that two sulfide ions are formed for each thiosulfate ion produced.

If an oxidation of disulfide is carried out slowly no appreciable amount of thiosulfate is formed until the system is saturated with sulfur. On the other hand, in the normal case where equal concentrations of sulfide ion and nitro compound are added together at the start, about 30% of the initial sulfide is oxidized in the first minute—Table II. Under these conditions there is a large amount of sulfur present in the "active" state at any particular time during the first few minutes. This sulfur would normally be dissolved by the sulfide ion still present but the large concentration of hydroxyl ion also present slows down this process and forms thiosulfate and regenerates polysulfide from the "active" sulfur. In the presence of other anions, as when neutral salt is employed, some of the sulfur is precipitated in solid form. This redissolves, in part at least, unless temperatures lower than 25° prevail. At higher temperatures the sulfur held in the polysulfide ion is more reactive and thiosulfate is formed at a much lower value of the ratio $xS/S_x^=$. Tartar and Draves[7] have shown that this ratio may be less than one with excess hydroxyl ion at 100°.

Summary

The oxidation of sulfide ion by means of an aromatic nitro compound progresses only as far as free sulfur. This sulfur is then removed from the system either by the formation of thiosulfate ion with regeneration of polysulfide ion or the sulfur is precipitated in solid form.

Thiosulfate ion is formed from free sulfur in the presence of hydroxyl ion with the simultaneous formation of two polysulfide ions. This reaction progresses slowly at room temperature unless the sulfur is in an active form.

Various ortho, meta and para substituted mononitro compounds were used as oxidizing agents and their rates of oxidation compared.

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(7) Tartar and Draves, THIS JOURNAL, 46, 574 (1924).

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Electrical Conductivities of Mixtures of Sulfuric Acid, Acetic Acid and Water

BY NORRIS F. HALL AND HERVEY H. VOGE

Introduction

As part of the general program of acidity studies from this Laboratory, a rather careful investigation has been made of the highly acid homogeneous system: sulfuric acid, acetic acid, water. The study has included measurements of conductivities, electromotive forces, vapor pressures and colorimetric measurements. Some freezing points have been determined, and the results of others recalculated. Other investigators who have recently studied certain aspects of this problem include Hall and Conant,[1] Hall and Werner,[2] Hantzsch and Langbein,[3] Hutchison and Chandlee,[4] Hammett and Deyrup,[5] James Kendall,[6] La Mer and Eichelberger[7] as well as Dr. Sprinkle and Mr. Freeman of this Laboratory.

The present paper describes the conductance measurements, and is divisible into three parts: (I) the conductance of dilute solutions of sulfuric acid in acetic acid; (II) concentrated solutions, and (III) conductivities in the ternary system sulfuric acid–acetic acid–water.

I. Dilute Solutions

A. Apparatus and Materials.—The resistances were measured by means of a Jones[8] bridge manufactured by Leeds and Northrup. A simple Hartley oscillator with a 201A tube, operating at 1400 cycles per sec., was used, as well as a two-stage transformer-coupled audio frequency amplifier and head phones. The oscillator and amplifier were separated from the bridge and each other and (with all leads) completely shielded. Absolutely silent minima and precisions of the order of 10^{-6} were readily obtained. Standard Oil Company "Finol" was used in the thermostat, which was heated by a bare wire and controlled by a mercury-in-glass regulator with oscillating contact. The bath was set at 25 ± 01° with a B. S. standard thermometer and held a constant temperature within 0.005'. The cells were made of glass with platinum electrodes and were of the usual design. Their constants were obtained by means of the 0.01D solution of Parker[S] prepared from "equilibrium" water and purified potassium chloride. Solutions were made up and kept with every care to exclude moisture before and during the measurements.

Acetic acid was prepared by fractional distillation in an all-glass still of glacial acid obtained from the Niacet Chemical Company. That used had a melting point of 16.63° and a specific conductance (K) of 3×10^{-8}. In the course of its preparation freezing

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(1) Hall and Conant, THIS JOURNAL, 49, 3047 (1927).

(2) Hall and Werner, *ibid.*, S0, 2367 (1928).

(3) Hantzsch and Langbein, Z. *anorg. allgem. Chem.*, 804, 193 (1932).

(4) Hutchison and Chandlee, THIS JOURNAL. 53, 2881 (1931).

(6) Rammett and Deyrup, *ibid* . 64, 2721 (1932).

(6) Kendall, *ibid.*, 43, 1826 (1921).

(7) La Mer and Eichelberger, *ibid.*, 54, 2763 (1932).

(8) Jones and Josephs, *ibid.*, 50, 1049 (1928); see also Dike, *Rev. Sci.* Instruments, 2, 379 (1931)

(9) Parker. THIS JOURNAL, 46, 312 (1924).

points as high as 16.65" were recorded and values of κ as low as 1.05 X 10^{-8}. There is not a simple relationship between maximum freezing point and minimum conductance. This point is being further studied.

Sulfuric acid was obtained by mixing reagent quality fuming acid with 95% acid until a maximum freezing point of 10.46° was reached. This acid had κ = 1.02 X 10^{-2}, which may be compared to the values 0.97 X 10^{-2} obtained by Hantzsch and by Bergius,[10] and 1.04 × 10^{-2} obtained by Lichty.[11]

Acetic anhydride from Merck was fractionally redistilled. The corrected boiling point was 138.2" and κ = 1.94 X 10^{-7}.

B. Results.—The results are shown in Table I. No solvent correction has been made, and it is probable that none should be made. V is the molar dilution in liters, and λ is as usual $1000 V\kappa$. The results are calculated for sulfuric acid as a uni-univalent electrolyte as it certainly is in these solutions.[1,4,7]

In order to detect possible errors and because of the interest attached to such measurements, the effects of water and of acetic anhydride on the conductance were studied. For the former, acetic acid containing a very small amount of water *(0.08%* by the freezing point curve of Richmond and England)[12] was used as solvent. The results are shown in Table II.

TABLE I

CONDUCTIVITY OF SULFURIC ACID IN ACETIC ACID AT 25°

M. p. of solvent. 16.63"; sp. cond. 3 X 10^{-8}

Soln. no.	Concn. mole/l.	$\sqrt{\text{Concn.}}$	V, liter/mole	Sp. cond. κ X 10^6	Mol. cond.
1 d	0.924	0.9612	1.083	1531	1.653
2 d	.7345	.8570	1.362	856.1	1.165
3 d	.2220	.4712	4.505	26.52	0.1194
4 d	.1105	.3324	9.050	6.142	.0553
5 v	.1075	.3280	9.300	6.075	.05651
6 v	.02231	.1493	44.83	1.017	.04562
7 v	.01115	.1056	89.66	0.6274	,05625
8 v	.005576	.07465	179.3	.4012	,07194
9 v	.002788	.05287	358.6	.2848	.1021
10 v	.001394	.03732	717.3	.1943	.1394
11 v	.000697	,02644	1434 6	1468	,2105

TABLE II

THE CONDUCTIVITY OF SULFURIC ACID IN "WET" ACETIC ACID

M. p. of solvent, 16.47°; sp. cond. 8.2 X 10^{-8}

Soln. no.	Concn. mole/liter	$\sqrt{\text{Concn.}}$	V, liter/mole	Sp. cond. $\kappa \times 10^6$	Mol. cond.
1 v	0.08078	0.2842	12.38	6.21	0.07688
2 v	.04038	.2009	24.76	2.801	.06936
3 v	.02019	.1421	49.52	1.477	.07311
4 v	.01010	.1005	99.04	0.9279	.09189
5 v	.005048	.07106	198.1	.6113	.1212

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(10) Hantzsch, Z. *phys. Chem.*. *61*, 257 (1908); Bergius, *ibid.*, 72, 338 (1910).

(11) Lichty, THIS JOURNAL, 80, 1834 (1908).

(12) Richmond and England, *Analyst.* 51, 283 (1926).

Addition of acetic anhydride also caused an increase in the specific conductance. Thus a 0.119 *M* solution of sulfuric acid in acetic acid had κ = 7.21 X 10^{-6}, while when it was made 0.0357 *M* in acetic anhydride, κ rose to 8.01 $\times$ 10^{-6}. A 0.107 *M* solution of acetic anhydride in acetic acid had a κ of only 3.91 X 10^{-8}.

From these facts it is evident that the conductivities recorded in Table I are very near minimum values, and that the solutions contained neither water nor acetic anhydride in appreciable amounts. The data of Tables I and II and also those of Hantzsch and Langbein[3] and of Jones[13] are shown in Fig. 1. A possible reason for the difference between our results and those of the other investigators is suggested by our measurements on "moist" acetic acid solutions. Incomplete drying of the solvent produces just such a fairly uniform increase in conductance as is shown by the other measurements. In Fig. 1 the anomalous decrease of X with dilution (often previously noted for all types of electrolyte in this solvent) is clearly seen. The complete conductivity curve (not shown, *cf.* Fig. 3), also shows a maximum value of X in more concentrated solutions. These peculiarities have been discussed by Walden[14] and by Bjerrum[15] among others.

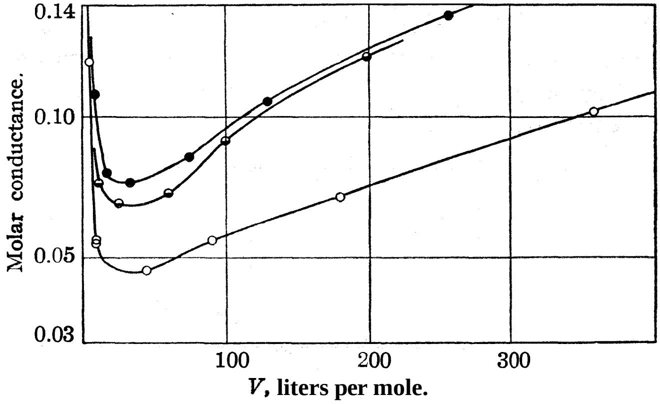

Fig. 1.—Molar conductance of sulfuric acid in acetic acid at 25°: ○, Voge; ⊖, *Voge*, solvent containing 0.08% H_2O; ●, Hantzsch and Langbein.

In the most dilute solutions the variation of λ with V is more nearly what would be expected from an ordinary weak electrolyte. A test of this type of behavior is furnished by a plot of CX against 1/λ.[16] If the Ostwald dilution law is obeyed, such a plot should yield a straight line from which both K and λ_0 might be derived. Figure 2 shows such a plot for the five

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(13) Jones, *Am.* Chem. J., 16, 1 (1894).

(14) Walden, "Leitvermögen der Lösungen," II, III.

(15) Bjerrum, Ber., 68, 1091 (1929).

(16) Kraus, "Properties of Electrically Conducting Systems." The Chemical Catalog Company. New York, 1922, p. 54.

most dilute solutions of Table I. It is seen that from the conductimetric viewpoint sulfuric acid is a typical weak electrolyte in the most dilute solutions. It is not possible, however, to determine λ_0 or K with any degree of precision from measurements on such high-resistance solutions as these. Even if the accuracy of the measurements were greatly increased this would not be possible. Walden[14] has given two useful generalizations which should establish the order of magnitude of λ_0. These are $\eta\lambda_0$ = const., and $\lambda_0\partial\lambda/\lambda\partial t$ = const. where η = viscosity and $\partial\lambda/\lambda\partial t$ is the temperature coefficient of the conductivity. By comparison with water as a solvent, these lead to the values $\lambda_0 = 280$ and $\lambda_0 = 70$, respectively, for the conductivity at infinite dilution of $H^+(HSO_4^-)$ in acetic acid. Use of these figures gives values for K ranging in the one case from 3.3 to 3.9 X 10^{-10} and in the other from 5.3 to 6.2 X 10^{-9}. While these figures are very approximate, they probably indicate the correct order of magnitude for the dissociation constant.

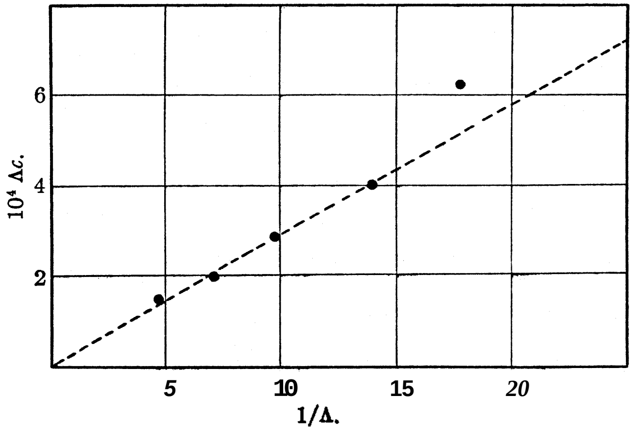

Fig. 2.—Sulfuric acid in acetic and the dilution law.

II. Concentrated Solutions and the Complete Conductivity Curve for the System H_2SO_4–CH_3COOH

This system has been investigated over a small range by Jones[13] and by Hantzsch and Langbein.[3] For these measurements a cell in the shape of an inverted Y was used which had a constant of 18.684 and to which varying amounts of liquid could be added without affecting the cell constant. The procedure adopted was as follows. The cell was cleaned, rinsed, dried at 140° and flushed with dry air. It was then weighed, filled with one component, and weighed again. The other component was added in successive portions from a weight buret, and the two were mixed in the glass-stoppered cell; after cooling at 25° in the thermostat, the conductivity was measured.

In Table III the results are shown Here the mole fractions are calculated from the weights in air against brass because of the low absolute accuracy. The conductivity curve is shown in Fig. 3, together with the viscosity curve of Drucker and Kassel.[17] It adds a little to the favorable evidence for the molecular compound AcOH·H_2SO_4 of which Kendall[6] finds indications in an unpublished freezing point curve, but which Lehrman could not crystallize.[18]

TABLE III

SPECIFIC CONDUCTANCES FOR THE SYSTEM H_2SO_4–AcOH AT 25°

Soln. no. n	Mole fract. H_2SO_4 N_2	Sp. cond. $\kappa \times 10^2$	n	N_2	$k \times 10^2$
1	0.000	0.00265	11	0.372	1.113
2	.01282	.00265	12	.404	1.139
3	.04155	.08561	13	.523	1.540
4	.0520	.1531	14	.639	2.945
5	.1133	.6658	15	.737	5.394
6	.175	1.009	16	.835	7.450
7	.258	1.128	17	.929	7.116
8	.277	1.126	18	.960	5.452
9	.307	1.116	19	.990	2.573
10	.325	1.111	20	1.000	1.0

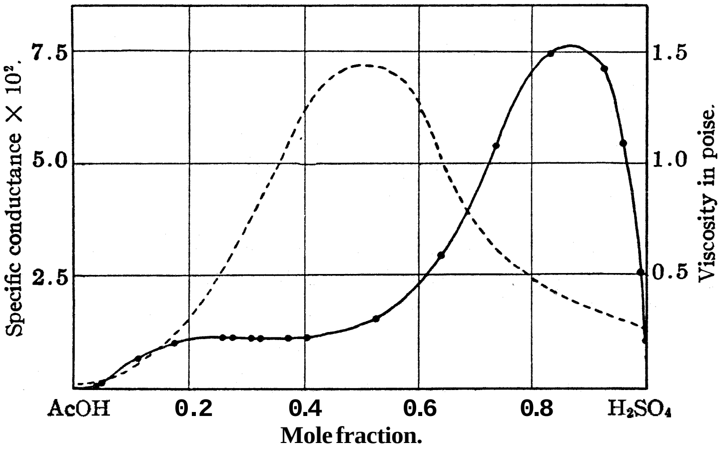

Fig. 3.—Conductance and viscosity of AcOH–H_2SO_4 mixtures: ——— specific conductance curve for the system H_2SO_4–AcOH at 25°; – – – – viscosity curve from Drucker and Kassel at 15°.

Complete explanation of the form of the curve is not possible, but the following factors may be pointed out. Solutions of acetic acid in sulfuric acid conduct better than those of sulfuric acid in acetic acid because of the much higher dielectric constant of sulfuric acid, although this must be

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(17) Drucker and Kassel, *Z. physik. Chem.*, 76, 367 (1911).

(18) Lehrman, Trans. *Am. Inst. Chem. Engrs.*, 18, 187 (1926).

partially offset by its greater viscosity. Equal rate of change of conductance in opposite directions caused by increasing concentration and decreasing ionization of acetic acid accounts for the pronounced maximum on the sulfuric acid side. The slight maximum on the acetic acid side doubtless has a similar explanation. The slight central minimum, while apparently arising from the increased viscosity at this point, cannot be separated in origin from the associative tendencies which cause the latter. Kendall[19] has given an excellent discussion of such systems and has pointed out our very incomplete knowledge of them.

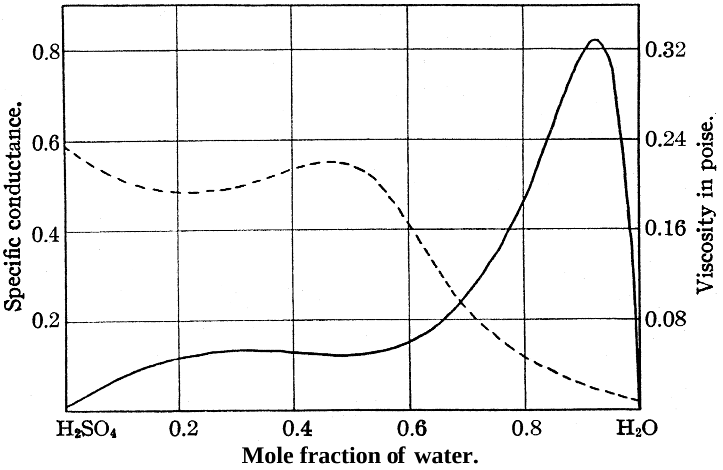

Fig. 4.—Conductance and viscosity of H_2SO_4–H_2O mixtures: ——— specific conductances for the system H_2SO_4–H_2O at 25° (Kohlrausch); — — — — viscosities for the system H_2SO_4–H_2O at 25° ("I. C. T.").

Conductivity curves[20] for the related systems H_2SO_4–H_2O and CH_3CO-OH–H_2O are of almost exactly the same form as that for this system. They are shown, corrected to 25°, and with their viscosity curves, in Figs. 4 and 5.

III. Conductivities for the Three Component System H_2SO_4–H_2O–AcOH

In the hope of more closely relating the highly acid solutions involved, and because of the rather novel interest attached to such measurements, the three component system H_2SO_4–H_2O–AcOH was next investigated conductimetrically. Almost no data exist on such mixtures; a few points of Jones[21] which lie quite close together and which were determined at an unspecified temperature are the only ones to be found in the literature.

In this portion of the research precision was less essential; hence the

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(19) Kendall, Ref. 6, and previous papers.

(20) Landolt-Bornstein, "Tabellen," H W II, pp. 1075–77.

following procedure was adopted. Mixtures of acetic acid and sulfuric acid were made up by weight in cell 7. Water was then added from a microburet, and on mixing and cooling to 25° the conductivity was measured. The composition of all mixtures was calculated from the weight in air.

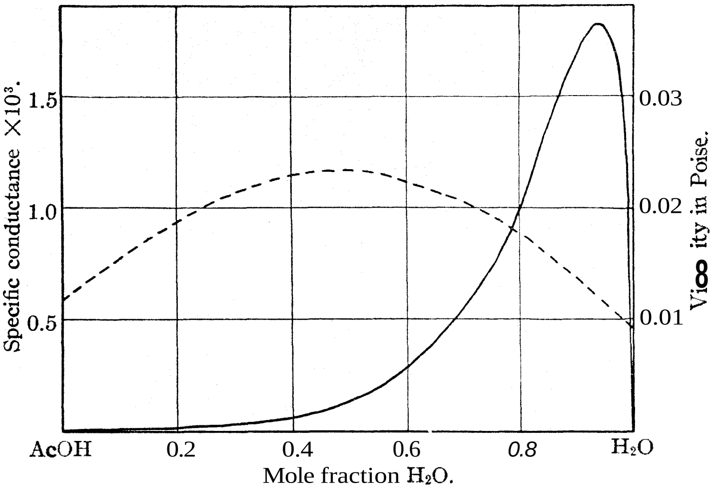

Fig. 5.—Conductance and viscosity of AcOH–H_2O mixtures: ——— specific conductances for the system AcOH–H_2O at 25° (Kohlrausch); - - - - viscosities for the system AcOH–H_2O at 25° ("I. C. T.").

Results are shown in Table IV, and in Fig. 6 by means of iso-conductive lines. This diagram indicates the interplay of the many factors determin-

TABLE IV

CONDUCTIVITIES IN THE SYSTEM H_2SO_4–AcOH–H_2O AT 25°

Series	No.	Mole fract. H_2SO_4	Mole fract. AcOH	Sp. cond. X 10^2	Series	No.	Mole fract. H_2SO_4	Mole fract. AcOH	Sp. cond. $\times 10^2$
I	1	0.210	0.709	1.180	IV	1	0.592	0.377	2.478
	2	.185	.625	1.397		2	.536	.342	2.568
	3	.140	.472	3.168		3	.470	.300	2.90
	4	.101	.341	8.09		4	.387	.246	3.99
	5	.079	.267	13.14		5	.316	.201	6.28
	6	.0646	.218	17.41		6	.252	.161	10.90
	7	.0475	.160	22.7		7	.194	.123	20.17
II	1	.350	.589	1.22		8	.150	.096	31.3
	2	.266	.449	2.21	V	1	.830	.120	6.654
	3	.204	.344	4.82		2	.751	.109	6.56
	4	.152	.256	11.02		3	.667	.097	6.29
III	1	.469	.454	1.598		4	.599	.087	6.13
	2	.419	.406	1.93		5	.527	.076	6.26
	3	.371	.360	2.429		6	.404	.0585	8.60
	4	.314	.305	3.567		7	.316	.046	14.01
	5	.249	.242	6.653		8	.196	.028	33.7
	6	.167	.162	14.44					

ing conductivity in such solutions. Here the trough may be related to loose compound formation or other associative phenomena, while the maxima serve to indicate roughly the points of greatest ion concentration. More complete explanation of these conductivities is not possible at present.

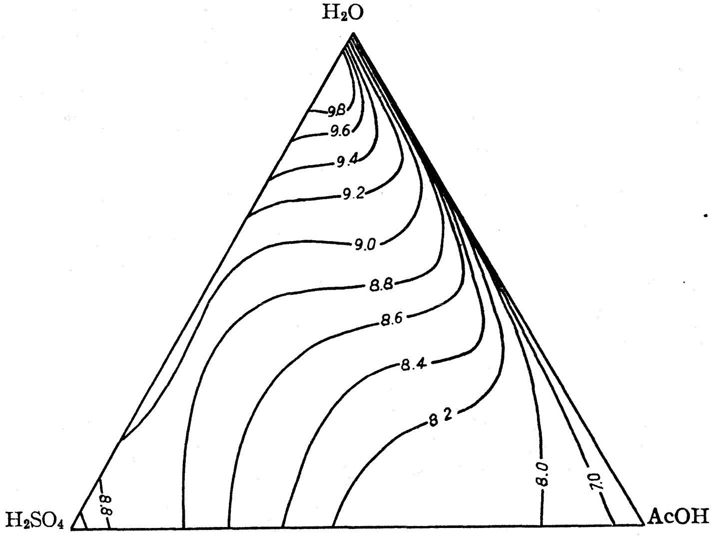

Fig. 6.—Iso-conductive lines showing log specific conductance + 10 for the system H_2SO_4–H_2O–AcOH at 25°; concentrations are in mole fractions.

Attempts to extend the study to the more general system SO_3–H_2O–Ac_2O were not successful. On adding acetic anhydride to 30% fuming sulfuric acid, chemical reaction took place and the solution turned orange in color. It was noted that the resistance was increased on adding the acetic anhydride but no quantitative conclusions could be drawn. These data will be discussed further in later papers dealing with the thermodynamic properties of the system.

Summary

1. The conductance of dilute solutions of sulfuric acid in acetic acid has been carefully redetermined. It is shown that the solute behaves as a typical weak electrolyte and its dissociation constant is tentatively calculated as 10^{-9}.

2. The complete conductance curve is determined for the binary system H_2SO_4–CH_3COOH and discussed in connection with similar curves for the systems H_2SO_4–H_2O and H_2O–CH_3COOH.

3. The complete conductance diagram is given for the system H_2SO_4–CH_3COOH–H_2O.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Galvanic Cells Containing Potassium Triphenylmethyl

BY H. E. BENT AND E. S. GILFILLAN, JR.

One of the most interesting properties of organic free radicals is the reaction with an alkali metal to give a compound having many of the properties of a simple salt. Such a compound will react metathetically with an acid (*i.* e., a methane),[1] will dissolve to give a solution which is an electrolytic conductor[2] and is formed with the liberation of an amount of energy not greatly different from that accompanying the formation of a typical inorganic salt.[3]

In spite of the salt-like character of these compounds we have been able to find no records of experiments in which solutions of them have been used as electrolytes in galvanic cells. Should they behave as normal salts in such experiments they would supply just the required properties for solving the problem of determining the standard electrode potential of cesium. The measurements would consist in determining the potential of a cell composed of electrodes of cesium and a dilute cesium amalgam and then the potential of another cell containing this same amalgam in contact with cesium ion in aqueous solution.[4]

In order to determine the suitability of these compounds for use in galvanic cells we have studied the behavior of cells in which the electrodes were potassium and potassium amalgam and of cells containing two electrodes of dilute amalgams. The electrolyte in these cells was a solution in diethyl ether of the potassium addition compound of triphenylmethyl or a closely related compound containing biphenyl or naphthyl groups.

Our experiments show that cells which have potassium amalgams for both electrodes give potentials which one would expect for a normal salt, *i.* e., the same potential as is found when the electrolyte is potassium iodide dissolved in ethylamine or potassium hydroxide dissolved in water. However, cells containing one potassium amalgam electrode and one potassium electrode give very erratic potentials which are less than correspond to the transfer of one gram atom of potassium for each Faraday of current. A number of cells designed to determine the cause of this behavior show that it is not due to impurities in the electrodes or to surface effects but to some change in the electrolyte which takes place in the presence of potassium.

These observations indicate that these compounds are quite unsuited to the problem of determining the cesium electrode potential. They also

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[1] Conant and Wheland, THIS JOURNAL, 54, 1212 (1932).

[2] Schlenk and Marcus, Ber., 47, 1664 (1914); Ziegler and Wollschitt, Ann., 479, 123 (1930).

[3] Bent, THIS JOURNAL, 52, 1498 (1930).

[4] Lewis and Kraus, *ibid.*, 32, 1459 (1910).

suggest that a cell reaction cannot be taken for granted in determining potentials. Finally these results further justify the assumption that these compounds are simple salts except when undergoing a transformation in the presence of alkali metal.

Experimental

Eleven cells have been prepared and their potentials measured. A Wolff potentiometer and a Leeds and Northrup type HS galvanometer, which is sensitive to 10^{-11} ampere, were used. In general the technique consisted in evacuating the cell until the pressure was too small to be measured on a McLeod gage (less than 10^{-4} mm. of mercury), distilling the potassium into the cell, introducing the amalgam by means of a stopcock, and introducing the electrolyte by breaking the tip of a glass capsule with a magnetic hammer.

In order to test the materials and method of assembly, one cell was prepared as nearly as possible like the ones used by Lewis and Keyes in the determination of the standard electrode potential of potassium;[5] *i. e.*, potassium | potassium iodide in ethylamine | 0.2216 weight per cent. potassium amalgam. The e. m. f. obtained by Lewis and Keyes was 1.0481 volts. We obtained a value of 1.0487 ± 0.0002 volts using an amalgam containing 0.2216 weight per cent. potassium. This agreement indicates that the method of handling the materials is satisfactory.

The evidence that potassium addition compounds of free radicals behave in a perfectly normal manner in cells containing amalgam electrodes is furnished by the data from three cells. The first of these cells furnished the best evidence. It was constructed to give a very low resistance in order to give very high accuracy in the e. m. f. measurements. It consisted of a tube twenty centimeters long containing a ridge the length of the tube, formed by pushing in the glass with a copper tool. The amalgams extended the length of the tube but were kept separate by this ridge. The tube was then nearly filled with the ether solution of potassium triphenylmethyl. The e. m. f. could be measured to two one-hundredths of a millivolt and was found to be 0.12835 ± 0.0002. Amalgams from the same storage flask were then used in another cell of the type used by Richards and Conant,[6] using as electrolyte an aqueous solution of potassium hydroxide. The e. m. f. so obtained was 0.12835 ± 0.0001, in perfect agreement with the value previously obtained.

A second cell with amalgam electrodes was constructed to test the behavior of other organic free radicals and different methods of preparing the potassium addition compound. The electrolyte was prepared by treating a mixture of methyl diphenylbiphenylmethyl ether, methyl α-naphthyldiphenylmethyl ether and methyl-α-naphthylphenylbiphenyl methyl ether with metallic potassium. The observed e. m. f. was 0.0291 ± 0.0001. The value found for the same amalgams when using a solution of potassium iodide dissolved in ethylamine as the electrolyte was 0.0291 ± 0.0001. Here again the agreement is within the experimental error.

A third cell which was designed primarily for a different purpose gave still further proof that in such cells the electrolyte is behaving in a perfectly normal manner. The e. m. f. found was 0.0655 ± 0.0005. The value found with potassium iodide dissolved in ethylamine as the electrolyte was 0.0652 ± 0.0001.

Eight cells were constructed which contained one amalgam electrode and one electrode of potassium. With the exception of one cell which was doubtless defective[7]

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[5] Lewis and Keyes, THIS JOURNAL, 34, 119 (1912).

[6] Richards and Conant, *ibid.*, 44, 601 (1922).

[7] The defective cell gave very erratic potentials and soon exhibited so high a re-

the e. m. f. was always too low and was inconstant. Most of these cells could be measured with an experimental error of not more than 0.01%. However, the e. m. f. was from 0.5–0.95 of the correct value and usually decreased during a period of a week or two by 10–20% of its value.

The construction of these cells will not be discussed in detail. However, in their construction the following factors were considered as possibly related to their behavior: surface films on the potassium; mercury dissolved in the surface layer of potassium coming from the pump, amalgam or electrolyte; a change in the concentration of amalgam due to transfer of potassium; polarization; and the nature of the free radical. In addition cells were constructed which differed greatly in resistance. The concentration of the electrolyte was varied from a highly supersaturated solution to one whose mole fraction was 10^{-7}. This very high dilution was accomplished by decantations in a closed system and subsequent distillations of the ether back into the cell The effect of time was studied by making measurements within a few seconds of the time of contact with the potassium and extending the measurements for a period of months. In order to avoid the possibility of traces of mercury from the solvent contaminating the potassium, the electrolyte was prepared in the absence of mercury. The usual way of making the electrolyte was to shake a solution of triphenylchloromethane with dilute potassium amalgam. In order to avoid the presence of mercury and vary the method of preparing the electrolyte, three ethers were prepared and then treated with metallic potassium. The reaction required five weeks for completion, the solution being shaken mechanically during this period. The resulting solution did not differ in appearance from solutions prepared from the chlorides. These ethers have apparently not been described in the literature. They were prepared by dissolving the chlorides in benzene, adding methyl alcohol and recrystallizing the products from dry ether. The three compounds were methyl diphenylbiphenylmethyl ether, m. p. 94–95", methyl diphenyl-α-naphthylmethyl ether, m. p. 142°, and methyl-phenyl-a-naphthylbiphenyl ether, m. p. 190–191°.

The last cell which we constructed seems to shed the most light on the behavior of these cells. This cell contained three electrodes, two of dilute amalgams and one of potassium. The electrolyte was introduced in such a way as to come in contact with only the amalgams. The observed e. m. f. was 0.0655 ± 0.0005. The correct value is 0.0652 ± 0.0001. The cell was then tipped so that electrolyte came in contact with all three electrodes. As was to be expected, the value obtained using the potassium as one electrode was too small. However, the value obtained using the two amalgams was changed to 0.0605, a difference ten times the experimental error of measurement. Tipping the cell so as to remove the electrolyte from the potassium did not alter this value but after three weeks a value of 0.0599 was obtained. Further standing in contact with potassium resulted in a value of 0.0523. This cell indicates clearly that the electrolyte undergoes some slow irreversible reaction such that the cell reaction is no longer the transfer of one gram atom of potassium for each faraday of current passing through the cell.

Conclusions

1. Potassium triphenylmethyl and some related compounds function as normal electrolytes in galvanic cells containing amalgam electrodes.
2. Potassium triphenylmethyl and some related compounds undergo a slow irreversible reaction when in contact with potassium which precludes their use in galvanic cells containing potassium.

CAMBRIDGE, MASSACHUSETTS

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sistance that it could not be measured. We presume that the potassium pulled away from the connecting wire during solidification.

Notes

Improved Method of Sealing the Capillary Tubes in the Rast Modification of the Barger Method of Molecular Weight Determination

BY JOSEPH R. SPIES

In the determination of molecular weights by the Rast modification of the Barger method it has been found that by operating in the manner described below the comparatively large air space at one end of the capillary tube and also the necessity of twice drawing out one end of this capillary can be avoided. The method has the further advantage that the liquid is fixed in both ends of the capillary without heating the capillary close to the enclosed solutions. This minimizes the danger of volatilizing some solvent or possibly decomposing some of the solute.

Assume that the standard solution and the test solution have been introduced into the capillary with the prescribed 3 4 mm. air space separating them, and that the tube has been melted shut on the right and drawn out 2 cm. to hairbreadth on the left as Rast describes.[1] Now instead of breaking off the left end at the end of the hair, it is allowed to remain, leaving a funnel-shaped reservoir. The tube then appears as illustrated in Fig. 1. The right end is now broken off and the tube tilted so that the liquid flows back through the hair to a position "a." The tube is then drawn out on the right to hairbreadth for 2 cm., broken at the end of this hair and tilted so that the liquid runs into and fills it, whereupon it is sealed by carefully touching it in a micro flame. Some of the liquid should remain in the funnel on the left so that the hair on the left is still filled. This funnel is then broken off and the end of the hair passed rapidly through a micro flame to expel a small portion of the solution before sealing as on the right.

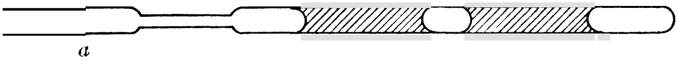

Fig. 1.

A 5 × 17 cm. glass plate with a line etched through the center parallel to the short side supplants the 1–2 X 17 cm. plate used by Rast. This allows eight to ten tubes to be placed on one plate. The etched line takes the place of the hair covered with Canada balsam. When it stands in water, balsam gradually becomes opaque and must be replaced daily.

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(1) K. Rast, *Ber.*, 54, 1979–1987 (1921).

The Dielectric Constant of Solid Hydrogen Sulfide

BY J. D. KEMP AND G. H. DENISON

Preliminary measurements have been made on the variation of the dielectric constant of solid hydrogen sulfide with temperature. Heat capacity measurements made in this Laboratory by Professor W. F. Giauque and Dr. R. W. Blue[1] have shown the existence of three crystalline modifications of hydrogen sulfide. It was therefore of interest to learn whether any rotational motion of the electric moments of the molecules in the crystal was taken up at the transitions.

A heterodyne beat method similar to that described by Zahn[2] with the oscillators operating on a wave length of 649 meters was used for the measurement of the dielectric constant. The test condenser (cap. 150 $\mu\mu$f) consisted of three concentric cylinders of gold rigidly separated by four glass rods cutting diametrically through them. The condenser was sealed in a glass cylinder and the temperature controlled by an apparatus similar to that used by Giauque and Wiebe,[3] the gold condenser replacing their calorimeter. A copper–constantan thermocouple was used for the temperature measurement.

The value of the dielectric constant below the lower transition at 103.5° K. is about 2.9 and above the lower transition for the second modification about 9, a discontinuous change taking place at the temperature of the transition. At the upper transition at about 126.3°K., there is apparently no marked change of the dielectric constant taking place. The value of the constant for the liquid at the melting point 187.6°K. is about 9.4. The accuracy of the measurements in the solid state is probably no better than 10% due to the effect of the large cracks encountered in warming the hydrogen sulfide.

From the results given above it appears that there is little or no rotation of the electric moment of the hydrogen sulfide molecule below the lower transition. At this transition a change in crystalline form must take place permitting rotation of the electric moments and from the large change in the dielectric constant it can be concluded that the molecules go from a state of little or no rotation of the electric moment to one of almost complete rotational freedom of the electric moment. This is further verified by the facts that at the upper transition there is no great difference between the dielectric constants of the two crystalline modifications of hydrogen sulfide concerned in the transition and that the value of the dielectric constant for the liquid at the melting point is of the same magnitude as the values for the crystalline modifications above the lower transition.

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(1) Not yet published.

(2) Zahn, *Phys. Rev.*, 24, 400 (1924).

(3) Giauque and Wiebe, THIS JOURNAL, 50, 161 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Number of Structurally Isomeric Hydrocarbons of the Acetylene Series[1]

BY DONALD D. COFFMAN, AND CHARLES M. BLAIR WITH HENRY R. HENZE

It has previously been possible, by means of a separation into types, arbitrarily chosen upon the basis of their structural formulas, to establish a relationship between the number of structurally isomeric hydrocarbons[2] and the alkyl groups of which the former may be considered to be composed. It can now be shown that an analogous method of separation into structural types may be utilized successfully in calculating the number of structurally isomeric hydrocarbons of the acetylene series.

The homologs of acetylene are divided into two groups: A, consisting of those hydrocarbons which may be formed, theoretically, by replacing one hydrogen atom of acetylene by an alkyl radical, and B, consisting of those which may be formed by replacing both hydrogen atoms of acetylene by alkyl radicals.

The structural formula of each of the homologs of acetylene of N carbon atoms of group A, R—C≡C—H, may be formed by replacing one hydrogen atom of acetylene by an alkyl radical of $N - 2$ carbon atom content. The total number of structural formulas that may be thus formed will equal the total number of alkyl radicals of $N - 2$ carbon atoms or $T_{(N-2)}$.

$$A_N = T_{(N-2)} \qquad \text{(A)}$$

The number of paraffin alkyl radicals of each carbon content through C_{20} has been previously reported.[3]

The structural formulas of the hydrocarbons of group B, R—C—C—R′, of N total carbon atom content may be formed by attaching to the —C≡C— group the alkyl radicals R— and R′— (the carbon content of R— plus R′— always equaling $N - 2$). The number of isomers that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the —C≡C— group every value of R—, taken one at a time, and every complementary value of R′—, also taken one at a time. These possibilities are theoretically of two types: (a), those in which the two alkyl radicals R— and R′— are of unequal carbon content; and (b), those in which the two alkyl groups are of

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[1] This joint contribution arose from independent and essentially concurrent efforts by the authors. The initial draft of Dr. Coffman's manuscript was presented to the editorial board of the Experiment Station of E. I. du Pont de Nemours & Co. on April *25, 1932,* and was approved by them for publication as a personal contribution. It was received in the office of the Editor of THIS JOURNAL on June 9; substantially identical results were presented on April *23* by C. *M.* Blair and H. R. Henze before the annual meeting of the Central Texas Section of the American Chemical Society at Waco, Texas, and their paper (Blair and Henze) was received by the Editor on June 18.—THE EDITOR.

(2) Henze and Blair, THIS JOURNAL, **53,** *3077 (1931).* It should be noted that the number of structurally isomeric nondecanes given erroneously as *147,248* in Table II, page *3084,* should be corrected to read *148,248,* as indicated by Perry, ibid., **54,** *2918 (1932).*

(3) Henze and Blair, ibid., 53, *3042 (1931).*

equal carbon content. In type (b) there may be further recognized two sub-types; (b_1), in which the two alkyl groups although of the same carbon content are not structurally identical; and (b_2), in which the two alkyl groups are structurally identical. Type (b) is actually impossible with a hydrocarbon of uneven carbon content, for in that type N − 2 should be divisible by two. The total number of isomeric homologs of acetylene of all types included in group B may be calculated by the following (finite) recursion formulas according to whether the carbon content is odd or even.

Odd:

$$B_N = T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \ldots\ldots + T_{(N-3)/2} \cdot T_{(N-1)/2} \qquad (B_o)$$

Even:

$$B_N = T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \ldots + T_{(N-4)/2} \cdot T_{N/2} + \frac{T_{(N-2)/2} \cdot [1 + T_{(N-2)/2}]}{2} \qquad (B_e)$$

Note that the subscripts in each term add up to $N - 2$, and that the number of terms is $(N - 3)/2$ for odd carbon atom content and $(N - 2)/2$ for even.

Table I indicates the number of structurally isomeric hydrocarbons of the acetylene series as calculated by the use of the recursion formulas.

TABLE I

NUMBER OF ISOMERIC HYDROCARBONS OF THE ACETYLENE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers
2	1	16	38,422
3	1	17	97,925
4	2	18	251,275
5	3	19	648,061
6	7	20	1,679,869
7	14	21	4,372,872
8	32	22	11,428,365
9	72	23	29,972,078
10	171	24	78,859,809
11	405	25	208,094,977
12	989	26	550,603,722
13	2,426	27	1,460,457,242
14	6,045	28	3,882,682,803
15	15,167	29	10,344,102,122
		30	27,612,603,765

Summary

1. Formulas of the (finite) recursion type are advanced which permit the calculation from their carbon content of the number of structurally isomeric hydrocarbons of the acetylene series. In using these recursion formulas to calculate the total number of such hydrocarbons of any given carbon content, the total number of alkyl radicals of N − 2 and all lesser carbon contents must be known.

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[CONTRIBUTION FROM THE DEPARTMENT OF MEDICAL RESEARCH, DETROIT COLLEGE OF MEDICINE AND SURGERY]

Technical Refinements for the Micro Colorimetric Method of Iodine in Blood

BY R. G. TURNER AND MINA Z. WEEKS

Several investigators are studying the determination of small amounts of iodine by use of the blue color formed with iodine and starch. Leitch and Henderson[1] and Aitken[2] oxidize the iodide to iodate with bromine, liberate the iodine by addition of an excess of potassium iodide and titrate with thiosulfate using the blue color produced by starch as the indicator. Aitken modified the method in that he devised a titration vessel in the form of a short tapering tube in which solutions can be brought with ease to a volume of 0.2 cc. Titration is made with $N/1000$ thiosulfate. In a later report[3] he recommends the use of a micro buret in which the standard solution floats on a thread of mercury, the position of the latter being adjusted by means of a fine screw projecting into a mercury reserve. Reith[4] and the author[5] have studied the same reaction, omitting the titration, comparing the color produced against known standards. Reith prepares several standards and matches these with the unknown, while in our method one standard is prepared and the unknown compared in a micro colorimeter. The stability of the color and its proportionality to the amount of iodine present have been found by the author[6] to be sufficiently accurate for the estimation of small amounts of iodine ranging from 0.0005 to 0.005 mg.

During the course of our study certain difficulties have arisen. At times we have encountered a complete failure, either slight or no color developing or an intense black color resulting. These two difficulties have been overcome by the use of special purified reagents The purpose of the paper is to give in detail the factors which we have found to cause failures and the necessary procedures to overcome these difficulties.

Experimental

The first difficulty encountered with the method was a partial or complete failure of color development. Reith (personal communication) wrote that iodine is lost if added to alcohol and the alcohol removed by ignition instead of evaporation. To 10 cc. of 94% alcohol he added potassium iodide sufficient in amount to bring the iodine content to 10γ. The alcohol was burned off and the iodine recovered was 0.7γ. Three

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(1) Leitch and Henderson, *Biochem. J.*, 20, 1003 (1926).
(2) Aitken, *ibid.*, 24, 1456 (1930).
(3) Aitken, *ibid.*, 25, 446 (1931).
(4) Reith, *Biochem. Z.*, 216, 249 (1929).
(5) Turner, *J. Biol. Chem.*, 88, 497 (1930).
(6) Turner. THIS JOURNAL, 52, 2768 (1930).

other experiments like the above were carried out with the exception that he added 2, 5 and 20 mg. of potassium carbonate. The results found were, respectively, 7.0, 7.4 and 10.1γ iodine. Therefore, he assumes that the alkalinity must be very marked before no loss of iodine occurs from ignition.

In the method described by one of us[5] it was stated that the absolute alcohol must be freed from traces of iodine by redistillation over potassium hydroxide. This practice worked successfully with some grades of alcohol but at times when new supplies of alcohol were used the development of color failed to appear.

The following experiments were undertaken to determine whether the failure encountered was due to ignition of the alcohol.

To two centrifuge tubes containing **50** cc. of water each, **0.001** and **0.002** mg. of iodine in the form of potassium iodide were added. Potassium sulfate and barium chloride were added as described in our method.[5] This was centrifuged and extracted and the solution evaporated to dryness in an oven. The dry residue was extracted with the non-redistilled alcohol and the alcohol btuned in a platinum crucible as described in the publication.

The above was duplicated in the same manner but instead of igniting the alcohol in the crucible, they were placed in an oven at 100° and allowed to evaporate. **The** residue in the platinum crucibles was then extracted with water as in the method given and a color developed. In both cases our results showed only a slight color not comparable with a 0 001-mg. standard.

Since both tests gave negative results it was thought that possibly some interfering substance such as aldehydes in the alcohol might have an inhibiting effect on color production. Alcohol was treated by the Winkler method[7] and by the method of Castille and Henri.[8] **A** modified form of the latter method has been adopted

Procedure for Purification of Alcohol.—One-half gram of iodine crystals is added to **500** cc. of absolute alcohol. The mixture is allowed to stand for twenty-four hours. Distil off the alcohol, discarding the first **25** cc. of distillate, and retain **50** cc. of the residue. Shake the distillate with **100 g.** of granulated zinc until the yellow color disappears. Distil off the alcohol again as above. To this distillate add as before **100** g. of granulated zinc and shake continuously for fifteen minutes. Distil as before. The alcoholic distillate thus obtained is free from iodine and interfering substances.

TABLE I

THE EFFECT OF PURIFICATION OF ALCOHOL ON COLOR PRODUCTION

Tube no.	Alcohol used for extraction	Results
1	Not purified	Negative
2	Purified by Winkler's method	Slight color but less than standard
3	Purified by modified method of Castille and Henri	Color equivalent to twice the standard or **0.002** mg. of iodine

If aldehydes are responsible for the interfering substance, they are not removed completely by the Winkler method. At present no claim is made

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(7) Winkler, Ber., 28, 612 (1905).

(8) Castille and Henri, *Bull. soc. chim. biol.*, 6, 299 (1924).

as to the identity of the interfering substance. Results have been satisfactory if the alcohol is treated by the iodine–zinc method as described. The experiment conducted to determine the possibility of loss of iodine by ignition of alcohol as described (on page 4) was repeated with alcohol purified by the iodine–zinc method. Complete recovery was obtained in both cases. Therefore, the failure of color production is not due to loss of iodine by ignition of the alcohol but to impurities which may be present in the alcohol and which are removed by the method presented.

The second difficulty in which the final reaction turned black due to oxidation of excess potassium iodide involves two factors. First, different samples of potassium carbonate may vary as to the amount of iodine present. The following method has been adopted for purification of all potassium carbonate used in the determination of small amounts of iodine.

Method for Purification of Potassium Carbonate.—To 100 g. of potassium carbonate in a liter beaker add 500 cc. of 95% alcohol. Stir with an electric stirrer for ten hours, decant the alcohol and dry the residue by pressure between filter paper. Dissolve the dried residue in 200 cc. of boiling water. Filter and evaporate the filtrate to one-third its original volume. Place in an ice-box to crystallize. When equilibrium is maintained filter and place the residue in an oven at 110° to dry. When dry powder and dissolve the contents in 100 cc. of hot water. Cool and pour the solution into a 500-cc. separatory funnel with an equal volume of absolute alcohol and shake continuously for thirty minutes. Transfer the aqueous layer to a 250-cc. beaker and evaporate over a flame to one-third its volume. Place in an ice-box until crystallization is complete, filter, and dry in an oven at 110°. Under these conditions no iodine could be detected in the purified potassium carbonate. 4 N potassium hydroxide may be used satisfactorily in place of the 4 *N* potassium carbonate solution. If chemically pure potassium hydroxide is used no purification is necessary.

Second, the iron content of the concentrated sulfuric acid used in preparation of the 2 N sulfuric acid solution must be taken into account. It is known that oxidized iron will set free iodine from potassium iodide. An investigation was made regarding the iron content of sulfuric acid and its effect on the starch–iodide reaction as used for the estimation of iodine in blood. One of the experiments is given as an example of the mode of investigation.

The following three samples of sulfuric acid diluted to the strength as used in the method (2 N H_2SO_4) were taken for examination.

Sample No. 1. Baker and Adamson containing 0.0002% iron

Sample No. 2. Baker and Adamson containing 0.00008% iron

Sample No. 3. Baker and Adamson reagent three months old. Iron content unknown. Tested negative when first prepared by the following method.

Method for Testing Purity of Sulfuric Acid.—Three drops of purified potassium iodide solution (1%) was added to each of three test-tubes (125 X 15 mm.) graduated to 1 cc. Distilled water (iodine-free) was added to the 1-cc. mark and 5 drops of the starch solution introduced. Two drops of sulfuric acid solution (No. 1 above) was added to tube No. 1. Likewise the same quantity of sulfuric acid solution (No. 2 above) was added to tube No. 2 and the sulfuric acid solution (No. 3 above) to tube No. 3. Another set of three tubes was prepared in a like manner with the exception that the 1% potassium iodide solution added had not been prepared with potassium iodide purified as described in our first publication.[5] These were numbered 1A, 2A and 3A, respectively.

The potassium iodide used in preparing the above solutions was Baker and Adamson (Lot 3A, Code Ba 4220). The results are shown in Table II.

TABLE II

THE EFFECT OF IMPURE REAGENTS ON COLOR PRODUCTION

Reagent no.	Color development Time in minutes 15	30	After addition of excess sulfuric acid reagent thirty minutes after development of the color Excess, 10 drops
1	+	++	+++
1A	++	+++	++++
2	−	sl +	sl +
2A	+	+	+
3	+	+	++
3A	++	++	+++

+ Equivalent to blue color produced with 0.001 mg. of iodine standard prepared as directed in the method. ++ Equivalent to a 0.002 mg. standard. +++ Dense, not matched against standards. ++++ Black, not matched against standards. sl + slight, not sufficient color to match against 0.001 mg. standard diluted to 2 cc.

The results show that if the sulfuric acid solution is fresh and sufficiently iron-free, no color is developed within fifteen minutes after adding the acid to the purified potassium iodide solution containing starch. The slight color produced at the end of thirty minutes with acid No. 2 (low in iron content) is believed to be due to the effect of the atmosphere on the oxidation of potassium iodide solution. This slow oxidation was recognized as stated in our publication[6] but if standard and unknown are prepared at the same time, the change is proportional for at least an hour and the colorimetric reading remains the same. The above experiment shows the effect of foreign oxidizable substance, presumably oxidized iron, on potassium iodide in acid solution. Potassium iodide is in excess when the final reaction for production of the color is carried out, therefore, the purity of the reagents used in this step must be watched. If foreign oxidizable substances are eliminated, iodine is not liberated from potassium iodide in acid solution within thirty minutes.

Conclusions

This investigation includes necessary procedures to avoid certain factors which cause failures in the author's method[6] for the estimation of iodine in blood.

To obtain satisfactory results it is essential to treat the absolute alcohol by the modified iodine–zinc method of Castille and Henri for removal of aldehydes.

Potassium carbonate must be freed from iodine by the method described or chemically pure potassium hydroxide used in its place to produce the desired alkalinity.

The sulfuric acid used for preparing the 2 N solution should not contain over 0.00008% iron, and at all times this reagent should be tested with the 1% potassium iodide solution for the presence of oxidizable foreign substance, assumed to be oxidized iron.

Under these conditions the above mentioned difficulties do not arise and the method of analysis can be carried through with the accuracy mentioned in the former publication.[5]

DETROIT, MICHIGAN
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Carbohydrate-Fatty Acid Linkings in Corn Alpha Amylose[1]

BY T. C. TAYLOR AND RUTH T. SHERMAN

The fatty acids associated with corn starch occur entirely in the *a*-amylose[2] or insoluble portion of the starch, while the soluble β-amylose is pure carbohydrate. Thus the presence of the fatty acids affords one means of differentiating between the two corn amyloses. In the interests of obtaining more data on chemical make-up of each of the corn amyloses, an examination of the linkage between the fatty acid groups and the carbohydrates in corn a-amylose is desirable. This investigation is concerned with that problem.

It has been shown that the fatty acid compounds in corn a-amylose are derived from palmitic, oleic and linolic acids,[3] which are chemically combined with carbohydrate for they are not extracted by solvents, but are liberated only after relatively long aqueous acid hydrolysis of the amylose.

In spite of the fact that these acids are in chemical combination with the carbohydrate, no corn a-amylose has been prepared which contains all that is in the original starch. Some is always lost in the process of separating the a-amylose from the β-amylose. This applies also to the derivatives of starch. Acetylated and methylated products of corn starch containing fatty acids have been prepared,[4] but in neither case do the products contain more than half of the original acids. This suggests that the fatty acids may not all be linked to the carbohydrate molecule in the same manner.

As starch is a polyhydroxylated compound, the fatty acids can be combined to the carbohydrate through an oxygen linking at any one or more of the otherwise free hydroxyl groups of the glucose residues which form the amylose molecule.

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(1) An abstract of a dissertation presented by Ruth T. Sherman to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

(2) (a) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); (b) Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

(3) Lehrman, "The Fatty Acids in Corn Starch and Synthesis of Corn Beta Amylose Palmitate," Columbia Dissertation, 1925.

(4) Werntz. "Studies of the Corn Amyloses," Columbia Dissertation, 1926.

The most direct and satisfactory way of determining the position of the fatty acids on the carbohydrate molecule would be to hydrolyze α-amylose to a glucose unit with the fatty acid radicals still attached and investigate the fragment. This cannot be accomplished at present, as the hydrolyzing agent splits off some fatty acids in the very early stages of hydrolysis of the starch.

Another method by which some light might be shed on the structure of corn α-amylose is to study the ease of removal of the fatty acids by hydrolysis. If the fatty acid residues are not all attached at the same relative positions on the glucose residues in the a-amylose, the stability of the starch–fatty acid linkages toward hydrolytic reagents ought not to be the same. Some linkages may be expected to be more easily broken than others, according to the methods of hydrolysis employed, if one uses the behavior under similar conditions of derivatives of glucose with substituents in various positions as a criterion. Here, in general, a substituent at position 1 in the glucose molecule is found to be the easiest to split off.[5]

The immediate purpose of this paper is to report the results of the effect of acid, alkali and enzymic hydrolytic reagents on corn α-amylose.

I. The Effect of Acid on the Liberation of the Fatty Acids from Corn Starch.—First, the preferential removal of these acid residues by a mild hydrolyzing agent, hydrogen chloride in 95% alcohol,[6] was studied. Samples of corn starch were treated with the reagent for different lengths of time, and the fatty acid content of the carbohydrate *residue* was determined.

After a given treatment the residue was freed from extraneous fatty acids and then completely hydrolyzed. Any newly liberated fatty acids were extracted and their iodine number determined. When this iodine value is compared with the iodine number of the fatty acids liberated by complete hydrolysis of the original starch, it is possible to determine the order in which the fatty acid groups are split off in the partial hydrolyses. If the iodine number of the acid in the residue increases, the palmitic acid must have been liberated more rapidly; if it decreases, the unsaturated acid linkings must have been hydrolyzed more readily than that of the palmitic acid.

Experimental

Five hundred cc. of a solution of 0.12 g. of hydrochloric acid in 95% alcohol was added to a suspension of 500 g. of corn starch in 500 cc. of alcohol. Samples of this mixture were heated under a reflux condenser on a water-bath for twenty minutes, forty minutes and one hour, respectively, after which they were filtered while hot on a suction filter and extracted for eight hours with ether. A weighed part of the treated

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(5) (a) Armstrong, *J. Chem. Soc*, **85**, 1048 (1904); (b) Will and Lenze, Ber., 31, 68 (1898); (c) Fischer, *ibid.*, 49, 584 (1916).

(6) By the use of alcoholic acid the amount of reducing sugar usually formed when aqueous acid is used is greatly diminished The alcohol also cuts down the tendency of the granules to swell and disrupt

starch in each case and a sample of untreated but ether-extracted starch was completely hydrolyzed with aqueous acid according to the method of Taylor and Nelson[2a] and the liberated fatty acids washed, dried, extracted, weighed and their iodine number found.

The iodine number was determined by the pyridine-dibromide method of Rosenmund and Kuhnhenn[7] except that after adding the pyridine-dibromide solution, the mixture was kept in the dark and shaken frequently, and that the excess of iodine was titrated with 0.05 N sodium thiosulfate solution.

The results are given in Table I. It can be seen that as the amount of the still-combined fatty acid in the treated starch decreases, its iodine number decreases. This shows that on treatment of corn starch with a mineral acid, the unsaturated acid radicals, oleyl and linolyl, are split more readily from the amylose than the saturated palmityl radical. The latter remains with the amylose and is only liberated when the amylose is more completely hydrolyzed.

TABLE I

THE EFFECT OF ALCOHOLIC HYDROGEN CHLORIDE ON THE FATTY ACID CONTENT OF CORN STARCH

Time of treatment	Fatty acid content of residue,[a] %	Iodine numbers	Av.
None	0.73	93.03, 93.09, 93.01, 92.66, 92.28, 92.51, 92.96	92.78
Twenty minutes	.44	73.07, 72.56, 73.36, 73.11, 72.78	72.97
Forty minutes	.21	53.64, 53.83, 53.71, 53.72	53.72
One hour	.059	27.51, 28.84, 26.75	27.37

[a] Average of two analyses.

II. The Effect of Basic Reagent on the Liberation of the Fatty Acids from Corn Starch.—In alkaline solutions, unmodified starch granules swell and form viscous pastes, but they still give a characteristic blue color with iodine after acidification. However, the fatty acid content of corn starch is greatly decreased by certain alkaline treatments. Rask and Phelps[8] report that heating corn starch for a short time with alcoholic ammonium hydroxide removes the fatty acids quantitatively, although in this Laboratory it has been shown that eight successive treatments with this reagent are needed before the fatty acid content of the starch becomes negligible.[9]

This reagent was used therefore in studying the action of alkaline reagents on the removal of the fatty acids from corn starch. In Table II will be found the results.

III. The Effect of Amylases on the Liberation of Fatty Acids.—The fate of the fatty acids in corn starch after treatment with an amylase has been reported in only one instance. Taylor and Nelson[2a] have found that on allowing corn starch to react with malt amylase, most of the fatty acids were liberated during the early stages of hydrolysis, but the amylase

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(7) Rosenmund and Kuhnhenn, Z. *Untersuch. Lebensm.*, *46*, 154 (1923).

(8) Rask and Phelps, *Ind. Eng.* Chem., *17*, 187 (1925).

(9) Taylor and Werntz, This JOURNAL, 49, 1584 (1927).

TABLE II

THE EFFECT OF ALCOHOLIC AMMONIUM HYDROXIDE ON THE FATTY ACID CONTENT OF CORN STARCH

Number of treatments		Fatty acid content of residue,[a] %	Iodine numbers	Av.
None		0.75	93.03, 93.09, 93.01, 92.66, 92 28, 92 51, 92.96	92.78
One	Sample I	.28	60.60, 60.67, 60.88, 60.83	60.74
	Sample II	.27	59.54, 59.71, 59.88, 59.67	69.70
Two		.18	46.13, 42.24, 46.23, 46.13	46.18
Three		**.13**	36.87, 36.90, 36.98, 36.90	36.91

[a] Average of two analyses.

preparation used by them had not been tested for fat-splitting enzymes. Any lipase present might be expected to hydrolyze the fatty acid compounds, irrespective of the action of the amylase. This will be demonstrated below.

In this work the action of a substantially lipase-free amylase on corn starch was investigated in order to ascertain its hydrolytic effect on the combined fatty acids. Should such an amylase attack the fatty acid bearing portion of the corn starch (the a-amylose), it could either split the carbohydrate, leaving the fatty acids combined with some product of lower molecular weight, or it could attack the carbohydrate–fatty acid linkages or both.

Corn starch was treated with several commercial amylases of different lipase content, in order to determine whether the presence of lipase will affect the quantity of fatty acid liberated during the course of the hydrolysis. The two most likely amylases were "Taka" diastase and "Superase."[10]

The lipase content of the enzyme was estimated by allowing the amylase to react on triolein and titrating the ether-extracted free oleic acid formed after the well-shaken samples had stood for twenty-four hours. The "Taka" diastase mixture was buffered at a P_H of 4.52 and held at 30° while the "Superase" was buffered at a P_H of 7.3 and held at 60°.

One sample of "Superase" liberated no oleic acid and another liberated about 0.5% while the "Taka" diastase liberated 1.5% of the acid. The first "Superase" sample is apparently substantially free from lipase.

Both the "Superase" and the "Taka" diastase were allowed to react with corn starch and the effect on the liberation of fatty acids studied. The results are given in Table III.

Experimental

Twenty-gram samples of starch were mixed with 100 cc. of cold distilled water and poured into 700 cc. of boiling water, taking care that no lumps were formed. To those samples containing the Taka diastase, 100 cc. of acetate buffer of P_H 4.52 was added; to those containing "Superase," 100 cc. of phosphate buffer of P_H 7.2–7.3. The samples were well stirred and kept in an oven for twenty-four hours. For those containing

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(10) (a) Furnished by Wallerstein Laboratories, 171 Madison Avenue, New York City. (b) Furnished by the Takamine Laboratory, Inc , Clifton. New Jersey, under the trade name "Clarase C."

"Taka" diastase the temperature was kept at 30°, and for those with "Superase," at 60°. They were then acidified with acetic acid until acid to methyl red, and a small quantity of mercuric chloride was added to each as a preservative. They were filtered through wet filter papers and washed with distilled water; the filter papers were dried overnight in an oven at 40°, and extracted for three days in a Soxhlet apparatus with ether and the residue in the flask weighed after evaporation of the solvent.

TABLE III

THE AMOUNT OF FATTY ACID HYDROLYZED FROM CORN STARCH BY THE AMYLASES

Amylase per 20 g. starch, g.	Fatty acid split by Taka diastase, g.	% of Total fatty acids split by Taka diastase	Fatty acid split by "Superase," g.	% of Total fatty acids in starch split by "Superase"
0.050	0.0162	12.2	0.0057	4.3
.100	.0244	18.4	.0075	5.6
.200	.0451	33.9	.0103	7.7

Fatty acid content of the starch, 0.73%. Time of treatment, 24 hrs.

From the results recorded in Table IV it is evident that the amylase containing lipase ("Taka" diastase) hydrolyzes the greater quantity of fatty acid from corn starch. The "Superase," which showed a practically negligible amount of lipase in the test on olein, also liberates the smallest amount of fatty acids from the corn starch.

When "Superase" is used directly on the corn a-amylose instead of the starch containing a-amylose there are similar results as shown in Table IV.

TABLE IV

THE REMOVAL OF THE FATTY ACID FROM α-AMYLOSE BY AN AMYLASE

Grams of amylase per 3 g. of a-amylose	Grams of fatty acid split from 3 g. of α-amylose		% Total fatty acid split	
0.050	0.0054	0.0048	4.5	4.0
.100	0.0060	0.0057	5.0	4.8
.200	0.0050	0.0056	4.2	4.7
.400	0.0078	0.0079	6.6	6.6
.600	0.0077	0.0083	6.5	6.9
1.000	0.0125	0.0127	10.7	10.7

The fatty acid content of the a-amylose was 3.8%.

Turning to the production of reducing sugar during this treatment, it was found in two preliminary experiments that when using. 0.05 g. of "Superase" per 20 g. of starch made as a 2% paste, the maximum amount of reducing sugar occurred after twenty-four hours. For example, when several 50-cc. aliquots of the mixture were titrated iodimetrically by the Willstätter–Schudel[11] method the reducing sugar expressed in milligrams of iodine per 500 mg. of starch (50-cc. aliquots contain 500 mg. of dry starch) was 170 and 171 for a twenty-four hour treatment and 169 and 170 for a forty-eight hour treatment.

By increasing the amount of amylase that acts on a given amount of

(11) (a) Willstätter and Schudel, *Ber.*, **51**, 780 (1918); (b) Goebel, *J. Biol. Chem.*, **72**, 801 (1927).

starch, the production of reducing sugar increases to a maximum for that concentration also at about twenty-four hours for optimum conditions.

That the degree of dispersion plays no essential part is shown by the fact that the results from ground corn starch[12] which disperses easily to give a limpid paste in hot water are practically the same as those from the thicker whole starch pastes.

As the ratio of "Superase" to starch is increased, a larger amount of fatty acids is liberated up to a certain point. Increasing the amount of "Superase" relative to the starch beyond that point causes no further splitting of fatty acid residues from the amylose.

The "Superase" produces reducing sugars from both corn alpha and corn beta amylose, so that its action on whole corn starch is not confined to the beta amylose alone. The average amount of reducing sugar from 500 mg. of whole starch is equivalent to 190 mg. of iodine and from the same weight beta amylose is equivalent to 202 mg. of iodine, but beta amylose constitutes only 85% of the whole corn starch.[2b] Therefore some of the reducing material must have come from the alpha amylose. During this breaking away of carbohydrate from the main portion of the alpha amylose under the influence of the "Superase" only a small portion of the combined fatty acids were freed.

Any residue, therefore, which is left unattacked will have a new ratio of carbohydrate to fatty acid which will be unlike the original. Beta amylose is completely hydrolyzed to reducing sugars so if whole corn starch is treated with "Superase" any unattacked residue must come from the α-amylose alone.

Acting on these observations a large amount of a 2% corn starch paste was treated with the requisite amount of "Superase" under optimum conditions for twenty-four hours and a residue obtained by centrifuging the mixture kept mold free with toluene. This residue after washing was dried, ground and extracted for ten hours in a Soxhlet apparatus with ether to remove any free fatty acids. Subsequently a sample of the oven-dry material was hydrolyzed completely with aqueous acid and the fatty acids liberated, extracted, weighed and their iodine number determined. This analysis of the carbohydrate–fatty acid compound showed that it contained a large amount of combined fatty acids, namely, 6.3%, whose iodine number was 60.7. The whole corn starch from which the alpha amylose had come showed 0.66% fatty acids (all in the alpha) whose iodine number was 95.8 while the alpha amylose separated from the same starch before the attack of the "Superase" contained 3.8% combined fatty acids.

Discussion of Results

In this work it has been shown that by the use of three methods, namely, hydrolysis by acid, by base and by amylase, the fatty acid groups com-

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(12) Taylor and Beckmann, THIS JOURNAL, **51,** 294 (1929).

bined with the α-amylose portion of corn starch are preferentially liberated. In all three cases the unsaturated acid radicals are the more easily removed. This result may be accounted for in two ways. It may be due either to a general lesser stability of compounds of carbohydrates with the unsaturated acids (oleic and linolic) in comparison with those of palmitic acid, or to the fact that these unsaturated acid residues are linked at positions different from that of the saturated one on the carbohydrate molecule. Position isomerism is known in the case of glucose derivatives to be the cause of differences in ease of hydrolysis.

Summary

1. The fatty acids associated with corn starch are hydrolyzed preferentially by acid, by base and by lipase-free amylase.

2. The linking between the unsaturated portion of the fatty acids and the carbohydrate is less stable to hydrolytic agents than that between the saturated portion and the carbohydrate.

NEW YORK CITY

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The Action of Aqueous Alkali on Starches, Amyloses and Modified Starches

BY T. C. TAYLOR AND G. M. SALZMANN[1]

The most common form of chemical change which starches or amyloses undergo gives rise to reducing sugars and is therefore probably a scission of glucosidic linkings. During the early stages of these transformations rather large changes in the physical aspects of the starches, or more particularly the pastes made from these starches, are obvious without any great accompanying changes in reducing value as measured by any of the common methods. By allowing the hot aqueous alkali to act on the sample, however, and then neutralizing and determining the new reducing matter iodimetrically by a modified Willstatter method,[2] it was found possible to magnify small differences among the starches and amyloses that would not be significant when based on the initial reducing value alone. This was possible because it was found that when any starch or amylose had an appreciable initial reducing value the aqueous alkali produced many times that amount after treatment.

While some inquiry was made into the nature of these reducing sub-

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(1) This is an abstract of a dissertation by G. M. Salzmann, presented to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Willstatter and Schudel, *Ber.*, **51**, 78 (1918); (b) Goebel, *J. Biol. Chem.*, **72**, 802 (1927); (c) Kline and Acree, *U. S. Bur. Standards J. Research*, **5**, 1063 (1932).

stances, the main purpose of this investigation was to use this alkaline treatment followed by an iodimetric determination of reducing material as a means of discovering whether this behavior toward hot aqueous alkali is a property of the original amyloses or is due really to some altered material admixed with the amyloses either as they occur in the starches or as they are isolated after disrupting the granules. The technique was employed further to find the type of treatment which would have to be given a starch or amylose so that it would give subsequently some material susceptible to aqueous alkali.

It will be shown that when a starch or amylose is modified, apparently only a part of the original polysaccharide is changed, the unattacked portion remaining stable to the alkali. The altered portion is completely broken down by the alkali but the stable portion is substantially nonreducing and similar to glycogen in its resistance to hot aqueous alkali. Original starch or amyloses with no history of hydrolytic attack from aqueous acid, enzymes, etc., are unaffected by repeated treatments with hot aqueous alkali and the amyloid material after such treatments is still like the original qualitatively by any of the criteria such as specific rotation, blue color with acidulated iodine-iodide test solutions and quantitative production of glucose.

It has been well established by Nef[3] and Evans[4] that glucose and maltose are decomposed by aqueous alkali, giving ultimately numerous non-carbohydrate substances such as pyruvic and lactic acids, etc. Many of these substances consume iodine under the slightly alkaline conditions that obtain in the iodimetric technique[2] employed here. The amount of iodine used up, however, is always much less than that used initially to oxidize the aldose. The breakdown with alkali through the enediol form of the glucose or maltose gives, according to Evans, the new products and obliterates the original sugar.

On the other hand, while the attack of alkali also begins apparently at the reducing group in a degraded amylose, the iodine consumption is always much *greater* after the treatment with hot aqueous alkali than it was initially.

Since aqueous alkali might give decomposition products in some enol form which would give fictitiously high reducing values,[5] some of the material after decomposition of the degraded amylose was allowed to remain acidified for one hour before the iodimetric determination was made. There was no change in the amount of alkali consumed.

Combination of the alkaline treatment with the iodimetric titration after neutralization gives a rather unique method of attack on the problem, the

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(3) Nef, *Ann.*, 357, 294 (1907); 376, 1 (1910).

(4) (a) Evans, Edgar and Hoff, THIS JOURNAL, 48, 2665 (1926); (b) Evans and Hutchman, *ibid.*, 50, 1497 (1928); *(c)* Evans and O'Donnell, *ibid*, **50**, 2550 (1928); (d) Evans and *Benoy, ibid.*, **52**, 294 (1930); (e) Evans, *Chem. Rev.*, 6, 281–315 (1929).

(5) Wolfrom and Lewis, THIS JOURNAL, **50, 837** (1928); Hudson, ibid., 52, 2101 (1930).

iodimetric method for determining reducing substances avoiding effects of alkali that the Fehling method would introduce and measuring somewhat more of the decomposition products than the copper method.

In establishing the optimum conditions for the estimation of alkali labile material in starches and amyloses it was necessary to find the effect of concentration of alkali and time of treatment on them. Since the iodine consuming material produced by the alkali is in the main unknown, all results are expressed in milligrams of iodine per 100 milligrams of sample, except glucose and maltose. Here, usually, a weight was taken that consumed as much iodine initially as the particular starch or amylose with which it was compared. Due to the production of acidic substances during the decomposition with alkali, the total available alkalinity at low concentrations (0.025 N) in the volume of solution used was insufficient but larger volumes of the same normality gave the expected results. At higher concentrations there was no difficulty even with small volumes of reagent.

Experimental

Fifty milligrams of the dry sample was added to 2 cc of water and to this mixture was added 2 cc. of a potassium hydroxide solution of such a concentration that the final mixture would have the desired normality with respect to the water. In a few cases where the total alkali was insufficient, 4 cc. of the aqueous alkali was taken but the normality of the mixture was fixed at the desired point by using the appropriate concentration of potassium hydroxide. The solution was placed in a large test-tube (8 X 1″) and the tube held in a boiling water-bath by a heavy asbestos board cover through which were bored holes just large enough to accommodate the test-tube. The test-tube was immersed in the water below the level of the cover, to a depth slightly greater than that of the contents of the tube. The purpose of this was to secure the maximum reflux action upon the walls of the tube. In *each case* the test-tube containing the alkaline mixture was heated for a definite selected length of time. At the end of the period the tube was removed from the bath, the contents transferred by washing into a 250-cc. Erlenmeyer flask, one drop of phenolphthalein solution[6] added and the solution neutralized with dilute hydrochloric acid.

For the titration, $N/20$ sodium hydroxide and $N/40$ standard iodine solutions were employed. As recommended by the Bureau of Standards[2] the iodine and sodium hydroxide solutions were added dropwise in four alternate portions using 3 volumes of the alkali to 4 volumes of the iodine solution. An excess of 2 or 3 cc. of iodine and 3 or 4 cc. of sodium hydroxide solution was usually added and the mixture allowed to stand about five minutes so that the total time before the back titration was twelve to fifteen minutes. After acidification with $N/5$ hydrochloric acid the excess iodine was titrated with $N/80$ thiosulfate solution. The presence of sulfuric acid or sulfates always led to recurring end-points and inconsistent results.

When using glucose in similar experiments, the sample was 3.4 g. which by iodimetric titration reduced 4.3 mg. of iodine. This amount was taken because in subsequent experiments its behavior with hot aqueous alkali was compared with that of the particular corn beta amylose which had an

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[6] Both the alcohol solvent and the phenolphthalein consume iodine so the minimum amount must he used. For very accurate work, say on glucose, it is better to use an aqueous solution of methyl orange which does not use up iodine [Mallen, *Analyst*, **54**, 244 (1932)]

initial reducing value of about the same amount. In this experiment, however, glucose and another corn beta amylose[7] were run.

The results are summarized in the graph, Fig. 1.

It is evident from the curve that there is always *more* iodine consuming material produced from the corn beta amylose than is initially present while with glucose there is always *less.* The maximum production from the amylose is with 0.1 *N* alkali while glucose is steadily decomposed at all normalities.

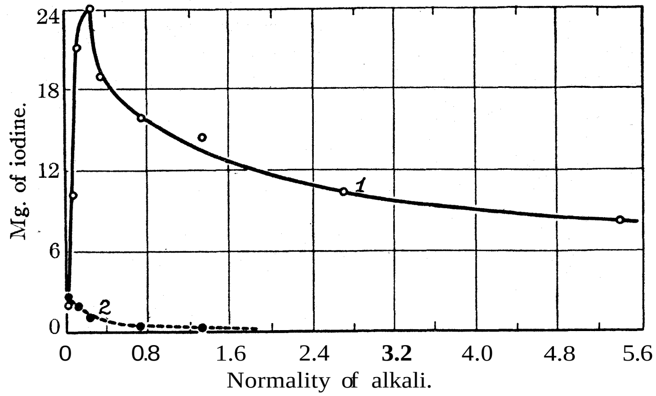

Fig. 1.—Reducing material expressed as mg. of iodine after treatment at normalities indicated: time constant at 15 minutes; Curve 1, corn beta amylose 100 mg.; Curve 2, glucose 3.4 mg.

To show that water alone has no effect, a sample of the beta amylose was treated for fifteen minutes and for two hours under conditions identical with the regular run but alkali was omitted. The reducing value was the same after the treatment as it was initially within the limits of the iodimetric determination.

Using 0.1 N solutions of potassium hydroxide a series of experiments was carried out on some corn beta amylose and on glucose in which the time of treatment was varied. This was done to see how the alkali effect changed when the treatment was prolonged beyond the fifteen-minute period. Each run was made for the specified time, the solution neutralized, cooled and the iodimetric titration made. The results are given in a graph, Fig. 2.

After a half-hour treatment the maximum amount of iodine consuming material is produced from this sample of corn beta amylose. Continued heating produces no more and after the one-hour period there is apparently some slight destruction of the reducing material already produced. On the other hand, glucose is decomposed to substances of less reducing value very early in the treatment.

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(7) Taylor and Beckmann, THIS JOURNAL, 61,294 (1929).

Although the maximum effect of the aqueous alkali is noticed with the 0.1 N concentration, many of the subsequent experiments were carried out using 5.45 N alkali because it was desired to make comparisons with the results obtained by McBride,[8] who used that concentration on glycogen in a similar set of experiments (this is the concentration of alkali used in the Pflüger method for glycogen isolation from tissue).[9] While the magnitude of the effect is not as great as with 0.1 *N* alkali, it is in the same direction.

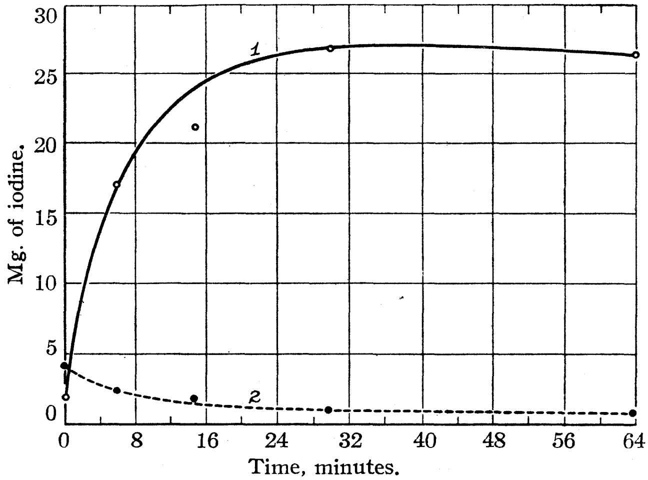

Fig. 2.—Reducing material expressed as mg. of iodine after treatment for periods indicated: normality of alkali constant at 0.1; Curve **1,** corn beta amylose 100 mg; Curve 2, glucose **3.4** mg.

To find out what the tendencies were when other samples were run with the 5.4 *N* alkali the following materials were taken: (a) corn beta amylose separated from ground starch by the electrophoretic method,[7,10] (b) corn beta amylose separated from alcoholic-hydrochloric acid treated corn starch after gelatinization and rupture with ammonium thiocyanate,[10] (c) corn white dextrin made by heating moist acidulated starch. This material has a rather high initial reducing value of 4.1 mg. of iodine. (d) A mixture of 100 mg. of corn beta amylose as in (a) with an initial iodine reducing value of 2.0 with 3.4 mg. of glucose with initial reducing value of 4.3 to make the total **6.3.** This was done to see if the method would discriminate between glucose and other reducing materials already present in the amylose. The complete record is shown in Fig. **3.**

It is interesting to note that there is more alkali labile material in the beta amylose separated from the acid-treated, thiocyanate gelatinized corn

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(8) J. J. McBride, Columbia Dissertation, 1929.

(9) *Arch.* ges. *Physiol.* (Pflügers), 93, 81 (1903).

(10) Taylor and Iddles, *Ind. Eng. Chem.*, 18, 713 (1926).

starch[10] than from that separated from the ground starch[7] or even a commercial white dextrin made by the dry heating of acidulated corn starch. As in previous experiments the glucose is quickly destroyed when alone and also when present with the beta amylose. After the first two minutes of the alkaline treatment the glucose is no longer a factor while the beta amylose runs its course as in the experiments without the presence of glucose.

These data point again to the fact that the initial reducing material in the amyloses and in the white corn dextrin is ***not,*** in the main, glucose.

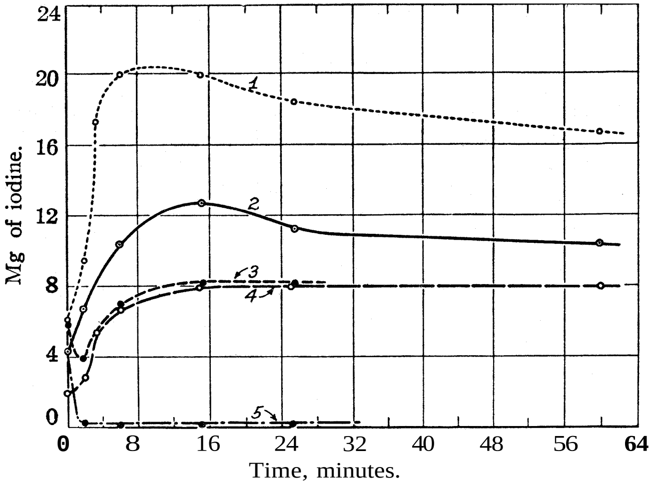

Fig. 3.—Reducing matter expressed in mg. of iodine after treatments of materials for period indicated with 5.4 *N* alkali: Curve 1, corn beta amylose from acid-treated thiocyanate-gelatinized starch; Curve 2, corn white dextrin; Curve 3, mixture of glucose, 3.4 mg., and corn beta amylose, the latter is the same material used in getting values in Curve 4; Curve 4, corn beta amylose from ground starch; Curve 5, glucose, 3.4 mg.; all amylose samples, 100 mg.

The reducing material present initially which is not glucose must be, therefore, closely allied to the amyloses and must have its source in them. It is probable that the reducing groups are the point of departure for the subsequent alkaline attack and the reducing material produced by this decomposition is substantially non-carbohydrate for it has no optical activity or other carbohydrate properties. In the absence of glucose the initial reducing value presages the amount of new reducing material which will be formed after the alkaline treatment.

That not all the starch or amylose is attacked by the alkali is shown by the fact that after neutralization of the alkali in any experiment, considerable quantities of starchy material may be precipitated by alcohol or, better, acetone. This slightly yellow precipitate when redispersed in water gives a clear blue color with acidulated iodine–iodide test solution and has a specific rotation practically the same as that of the original amylose. On complete acid hydrolysis this alkali stable residue yields glucose, quantitatively.

Either the precipitation method or the hydrolysis to glucose and subsequent iodimetric determination of it may be used to estimate the amount of amylose which is not susceptible to the attack of aqueous alkali. When concentrated alkali is used the latter method is somewhat better since a small amount of salt is precipitated with the amylose by the alcohol or acetone.

Experimental

The Precipitation Method.—1.250 grams of starch or amylose was placed in a 250-cc. Erlenmeyer flask to which was added 30–35 cc. of water, this mixture usually being warmed until a paste formed. To this was added 15 cc. of 0.4 N potassium hydroxide, which made the final solution approximately 0.1 N with respect to potassium hydroxide. The flask was then placed in a beaker two-thirds full of water and heated in this water-bath at 100° for one hour. When using whole starches, it was necessary to keep them for one and a half to two hours at 100° with 0.1 N potassium hydroxide instead of one hour, since it usually required one-half hour for the thick paste to become limpid and only after the production of this thin dispersion due to gelatinization and rupturing of the granules, does the alkali destructive action occur as evidenced by the production of the yellow color. After this treatment the flask was cooled and the contents slightly acidified with 2 N hydrochloric acid. Due to slow evaporation, the total volume was usually about 10–15 cc. less than at the start. To precipitate any unattacked amyloses 100 cc. of ethyl alcohol was now added. Vigorous shaking helped in coagulating the colloidal material. When a yellow dextrin was similarly treated, it was found that acetone gave a quantitative precipitation, which alcohol often fails to do. After the material had completely coagulated, which in some cases occurred almost immediately, while in others several hours of standing were required, the clear supernatant liquid was decanted off, the residue transferred to a mortar, ground using two 15-cc. portions of alcohol and twice washed with ether. This dried residue was placed in the oven at 60–70° for ten to fifteen minutes to remove traces of ether and then weighed. This weight represents the recovered amyloses after an alkaline treatment. Precipitations of hot water dispersed starch or amylose without an alkaline treatment were made so that the percentage recovery could be determined by proportion. For this purpose 1.250 g. of starch was placed in an Erlenmeyer flask to which 40–50 cc. of water was added. A dispersion was again made by heating, alcohol was subsequently added and the precipitated amyloses dried and weighed.

The "Hydrolysis Method" for Determining Alkali Stable Residue.—Fifty milligrams of the starch was placed in an 8-inch test-tube and dispersed in 1 cc. of water, to which was added either 1 cc. of 10.4 N potassium hydroxide or 1 cc. of 0.2 N potassium hydroxide, so that the final concentration of alkali would be approximately 5.4 *N* or 0.1 N with respect to water as desired in each instance. The mixture was kept at 100" for one hour in the water-bath, then cooled and neutralized with 2 N hydrochloric acid. To hydrolyze the remaining amylose 5 cc. of *2* N hydrochloric acid was added, and the tube placed in the water-bath at 100". It was found that hydrolysis was complete at the end of thirty-five minutes. The solution was cooled and neutralized with potassium hydroxide, and the reducing value determined in the usual way. This reducing value consists of the sum of the reducing value due to the glucose formed by acid hydrolysis, and the reducing material left after the action of the alkali. It will be shown later that this treatment with acid does not produce any change in the reducing material already present from the alkali treatment. In order to determine the reducing value due to the glucose from the unattached amylose, it is necessary to subtract from the total value the reducing value due to the alkali treatment.

To avoid any error in the percentage of amyioses stable toward the alkaline treatment, it is also necessary to make conversions of the same amounts of starch or amyloses to glucose, but with no alkali pretreatment. Fifty milligram samples of starch or amylose were hydrolyzed with 5 cc. of 5 *N* hydrochloric acid for thirty-five minutes and the reducing value in milligrams of iodine found. Then the percentage of unaltered residue could be calculated on the basis of the ratio of the glucose from the residue to the glucose from the original starch or amylose.

By multiplying the weight of glucose by the factor 0.9 a weight is obtained which is recorded as starch.

The precipitation method and the hydrolytic gave results that differed among themselves on repetition on the same sample by about 0.75%, and with one another from 2 to 4%.

The amount of alkali stable material in the particular samples used in the above experiments seems to vary according to the source of the sample. From whatever source they appear to be similar in character and all show an iodine consumption of one or two milligrams, due probably to adsorbed reducing material from the solution out of which they were precipitated. When subjected again to the hot aqueous alkali no appreciable change takes place even after heating with 0.1 N alkali for three hours. This is evident for no reducing material is formed in the presence of alkali, the amount of residue after the alkali treatment is substantially the same after this second treatment as after the first and the specific rotation and iodine color are the same as for samples of original starch.

To get some clue to the type of treatment that might cause a part of the starch or amylose to be converted to alkali labile material, a number of starches, amyloses and modified starches were investigated. The initial reducing value was determined, they were subjected then to hot aqueous alkali, neutralized and the new iodine consumption noted, after which the amount of stable residue was estimated. The results have been arranged in order of decreasing amounts of alkali stable fractions (see Table I).

There is an inverse relationship between the initial reducing value and amount of amylose remaining after the alkali treatment. Some samples of starch have practically no alkali labile material in them while others have more. This is due very probably to the method of manufacture and possibly to agricultural conditions under which the starch was grown. Of the definitely controllable factors aqueous acid is the most potent in producing alkali labile material although other conditions such as grinding the starch in a ball mill also cause degradation of a part of the amyloses as the results under items G and H in Table I show.

TABLE I

STUDY OF FACTORS INVOLVED AND RESULTS OBTAINED BY ALKALI TREATMENT OF STARCHES AND AMYLOSES

Sample	% Alkali stable residue by alcohol precipitation method	Initial reducing value of orig. substance on 100-mg. samples, mg. of iodine	Reducing value after 5.4 N KOH 1 hr. at 100° on 100-mg. samples, mg. of iodine
Potato starch, Sample A	97		3.3
Corn starch, Sample B	90		5.1
Ground tapioca starch, Sample C	83	1.4	4.6
Ground potato starch, Sample D	75	...	8.2
Lintner's sol. starch, Sample E	74	0.6	7.2
Corn beta amylose, Sample F	73	2.0	8.0
Ground corn starch, Sample G	68	1.9	8.8
Reground corn starch, Sample H	67	2.6	9.9
Corn alpha amylose, Sample I	62	1.6	9.6
Ground corn starch, Sample J	59	3.0	11.6
Corn white dextrin, Sample K	56	4.1	10.5
Thin boiling starch, Sample L	56	4.7	12.9
Ground potato starch, Sample M	51	2.2	12.8
Corn beta amylose, Sample N	49	6.0	16.8

NOTES

Sample A represents a good grade of commercial potato starch. Sample B represents a good grade of commercial alkali-washed corn starch. Sample C represents a tapioca starch which has been ground for eighteen hours with quartz balls in a ball mill.[7] Sample D represents potato starch which has been similarly ground for 120 hours.[7] Sample E represents Lintner's soluble potato starch made by keeping potato starch in contact with dilute hydrochloric acid for six days at room temperature and washing twenty-two times with water.[11] Sample F represents corn beta amylose, the soluble component of 168-hour ground corn starch after electrophoresis and precipitation.[7] Sample G represents corn starch ground for 168 hours. Sample H represents sample G ground corn starch which had been subjected to an alkali treatment, and reprecipitated out as the stable portion, which in turn was reground for another 140 hours in a small ball mill. Sample I represents corn alpha amylose, the insoluble component of 168-hour ground corn starch after electrophoresis.[10,7] Sample J represents 168-hour ground corn starch, reground another 160 hours in a small ball mill, so that the total time of grinding was 320 hours. Sample K represents corn white dextrin made commercially by spraying whole starch with dilute hydrochloric acid and heating this damp product around 180° for a short period of time.[12] Sample L represents a "thin-boiling" corn starch made by giving whole starch an acid treatment similar to that given Lintner's soluble potato starch.[12] Sample M represents potato starch ground for 500 hours in a ball mill. Sample N represents corn beta amylose made by treatment of corn starch with an alcoholic solution of hydrochloric acid, followed by an ammonium thiocyanate gelatinization.[10]

It is interesting to note that the iodine consuming value after a $N/10$ alkaline treatment is considerably higher than after the treatment with the more concentrated alkali as exemplified by samples as marked in Table II, giving for "C," 11.7 mg.; "F," 26.5 mg.; "G," 25.1 mg.; and "K," 36.5 mg.

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(11) Gore, *Ind. Eng.* Chcm., 20, 865 (1928).

(12) Walton, "A Comprehensive Survey of Starch Chemistry," The Chemical Catalog Co., New York, 1928.

Further, by grinding a corn starch and determining the alkali stable residue from time to time, it has been found that the effect increases with increase in time just as is the case in making "soluble" or "thin-boiling" starches by acid treatment in the cold. In the latter instance, of course the granules are not broken (see Fig. 4).

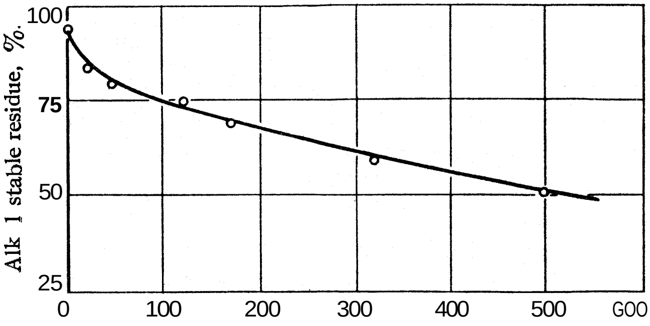

Fig. 4.—Relation between time of grinding of corn starch and amount of alkali stable residue.

The amount of surface exposed to the reagent at first in the case of the ground starch or amyloses is much greater than in the case of the soluble or modified starches where the granules are intact but the reagent soon swells and ruptures the latter, so conditions are about the same soon after the reaction has proceeded for a short time. Even a part of the less easily dispersed corn α-amylose[13,7,10] changes with acid treatment or grinding to give alkali labile material in a manner similar to the corn beta so that in the whole corn starch each of these amyloses is affected by various treatments to give alkali susceptible material. A sample of corn alpha amylose with an initial iodine reduction of 1.6 mg. per 100-mg. sample gave 10.9 mg. of iodine reducing material after a thirty-minute treatment at 100° in 5.4 N alkali.

When drying a sample of neutral ground starch already containing some alkali susceptible material, there was a slight increase in it (or decrease in alkali stable material). For example, when the initial alkali stable residue is 68.0% it changes to 67.0% after four hours, to 62.3% after sixteen hours, and to 61.5% after fifty hours at 105°.

On oven drying moist acidulated starch, which is essentially the process of white dextrin manufacture, there is, however, rather extensive breakdown of the starch, see Table I, item K. Apparently the acid causes this change during the early stages of the treatment when there is still considerable moisture present. Later if the temperature is raised, the white dextrin changes to yellow and a loss of water ensues. Finally no more

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(13) Taylor and Lifschitz, THIS JOURNAL, 54, 1054 (1932).

alkali labile material is formed, but on the contrary any alkali labile material already present is transformed over to alkali *stable*. This is illustrated rather strikingly by an experiment where a "thin boiling" starch containing but 56% alkali stable material (see Table I, Item L) was acidulated and roasted to make a yellow dextrin. This new dextrin contained 86% alkali stable material even though its initial reducing value was 10.6 mg. of iodine per 100 mg. of sample.

A rather large portion of the labile material must have been converted to some kind of stable material and the initial reducing value which normally would indicate a high alkali susceptible portion in an amylose must be in this case due to glucose or maltose or something similar to it for the high alkali susceptible portion does not materialize as it would in an amylose or starch with this initial reducing value. Some studies are being made now on the glucosan types in order to shed more light on these findings because the new stable material is not like the original amylose and synthetic dextrins from levo-glucosan are stable as is levo-glucosan itself toward hot aqueous alkali.

It must be remembered that every starch, amylose or dextrin whether it contains a large or small amount of alkali stable material will hydrolyze practically quantitatively to glucose on boiling with aqueous acid for a sufficient time. All these substances are therefore built up from glucose units whether they are alkali stable or alkali labile.

It is evident that starches and their amyloses may contain relatively large amounts of hydrolytically degraded but still very similar polysaccharides associated with them. While reducing in character this material is not in the main glucose or maltose and not truly water soluble although it may disperse. Pastes made from starches containing much of this material are less viscous than pastes made from the same weight of that same starch which contains but little of the partially broken down alkali-labile material. Such degraded starches are known as "thin-boiling" or "soluble starches." These changes may come about through enzymic attack before the starch is isolated, during the process of manufacture, or may be deliberately brought about by acid treatment as in making soluble starches, etc. The general appearance of the granule is substantially unchanged while these modifications are taking place in the amylose within.

When such partially degraded starches are used to make derivatives or as a substrate for enzyme action, it is probable that the speed and possibly the course of the reaction will be different with the two closely related but chemically different products. Such degraded products are very often employed for experiments on starch, for one of the first operations is often the "solubilizing" of the starch so that the pastes can be handled more conveniently. This lack of homogeneity throws some doubt on the results when these degraded substrates are used.

Another point of interest that develops from this work is the difference between the very alkali labile hydrolytic-type dextrins from the continued attack of the aqueous acid and the very alkali stable yellow dextrins from long roasting of starch. The two types of "dextrins" are obviously not the same chemically.

Summary

1. When a given starch, amylose or dextrin is heated with dilute or concentrated alkali, only a very definite fraction is destroyed by the alkali with a corresponding increase in the reducing value of the system as measured by the hypoiodite method.

2. Starch or amylose which has not been degraded is substantially unaffected by hot aqueous alkali.

3. Two methods are given for quantitatively estimating the portion of starch which is stable toward alkali.

4. Aqueous acid, certain heat treatment or grinding in the presence of moisture are capable of producing a high alkali unstable fraction from a given starch or amylose.

5. Yellow dextrin made by roasting starch contains a large amount of material stable toward alkali.

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The Interaction of Ketene with Aromatic Aldehydes and its Bearing on the Perkin Reaction

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

Shortly after discovering diphenylketene Staudinger[2] found that it would add to quinone and produce a β-lactone. Ketene itself failed to do this. Hence, this property of addition at carbonyl groups was ascribed to the disubstituted ketenes.

The present work concerns itself with the reaction of ketenes with aromatic aldehydes. From Staudinger's work it would be anticipated that no reaction should occur when ketene was passed into benzaldehyde. None was observed. If, however, a little anhydrous potassium acetate was present, ketene then reacted vigorously with benzaldehyde or furfural or m-nitrobenzaldehyde to produce dark colored, viscid liquids.

If the mechanism of the reaction consisted merely in direct addition, β-lactones should have been the major products. They were formed but the chief reaction products were mixed acid anhydrides, namely, cinnamic

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(1) Holder of a Quaker Oats Fellowship. 1929–1930, administered through the Miner Laboratories Chicago.

(2) Staudinger, *Ber.*, 41, 1355 (1908).

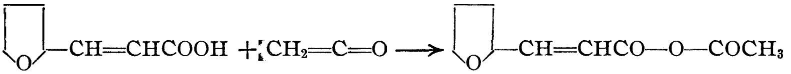
acetic anhydride, furylacrylic acetic anhydride and m-nitrocinnamic acetic anhydride. Such an effect may be summarized in the equation

$$\mathrm{ArCHO} + 2\mathrm{H_2C{=}C{=}O} \xrightarrow{\mathrm{KOAc}} \mathrm{ArCH{=}CH{-}CO{-}O{-}COCH_3}$$

Considering the reagents which are taken, this reaction with aromatic aldehydes, potassium acetate and ketene resembles the Perkin reaction which employs aromatic aldehydes, potassium acetate and acetic anhydride. This is obvious since both ketene and acetic anhydride give rise to acetic acid when treated with water.

Beta **Lactones** in the Reaction Product.—The presence of the β-lactones was established by pyrolysis. Styrene distilled from the benzaldehyde material and furylethylene[3] from the furfural material. The styrene could not have come from cinnamic acetic anhydride or from cinnamic anhydride for they were shown to pyrolyze differently. Furthermore, its forerunner could not have been cinnamic acid since it was not present and since the decomposition temperatore was lower than that required for cinnamic acid. Even milder conditions (steam distillation) were found to suffice in the production of furylethylene. In the case of the *m*-nitrobenzaldehyde reaction product, a small amount of liquid was formed as a product of pyrolysis. This may have contained m-nitrostyrene but it could not be established with certainty. Nor was it possible to isolate the β-lactone which, in this case, is known[4] to be fairly stable.

Synthesis and Reactions of Mixed Acetic Anhydrides.—Prior to the search for the mixed anhydrides in the reaction mixture they were prepared for study. The general method of Hurd and Dull[5] was used. Acetic cinnamic anhydride was prepared by passing ketene into a solution of cinnamic acid in ether. Acetic furylacrylic anhydride was prepared similarly from ketene and furylacrylic acid



Acetic furylacrylic anhydride is new and but little information exists regarding acetic cinnamic anhydride. Gerhart,[6] who prepared it from sodium cinnamate and acetyl chloride, reported it to be a very unstable oil. Using cinnamic acid and acetic anhydride, Autenrieth[7] obtained cinnamic anhydride but not the mixed anhydride.

Three reactions of acetic cinnamic anhydride were studied: (a) disproportionation into the symmetrical anhydrides. This occurred on distillation

$$2\mathrm{C_6H_5CH{=}CHCOOCOCH_3} \longrightarrow (\mathrm{C_6H_5CH{=}CHCO})_2\mathrm{O} + (\mathrm{CH_3CO})_2\mathrm{O}$$

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[3] Moureu, Dufraisse and Johnson, Ann. chim., 7, 14 (1927); *Bull. soc.* chim., 43, 586 (1925).

[4] Prausnitz, Ber., 17, 697 (1884).

[5] Hurd and Dull, THIS JOURNAL, 54, 3427 (1032).

[6] Gerhart, Ann., 87, 81 (1853).

[7] Autenrieth, Ber., 34, 186 (1901).

(b) reaction with phosphorus trichloride. Besson[8] reported the following reaction between acetic anhydride and phosphorus trichloride

$$(CH_3CO)_2O + PCl_3 \longrightarrow 2CH_3COCl + POCl$$

Repetition of this reaction showed that an 85% yield of acetyl chloride was formed. Similarly, the mixed anhydride was found to give an 85% yield of acetyl chloride with phosphorus trichloride

$$C_6H_5CH{=}CHCOOCOCH_3 + PCl_3 \longrightarrow C_6H_5CH{=}CHCOCl + CH_3COCl + POCl$$

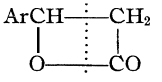
(c) analysis[5] with dry oxalic acid and pyridine. The reaction seems to hold quantitatively for the mixed anhydrides of the acetic type; *e. g.*

$$CH_3COOCOCH{=}CHC_4H_3O + (COOH)_2 \xrightarrow{C_5H_5N} CH_3COOH + \\ C_4H_3OCH{=}CHCOOH + CO + CO_2$$

It is not quantitative for all acid anhydrides, however, as cinnamic anhydride gave but nine-tenths of the calculated volume of gas and *m*-nitrocinnamic anhydride did not react at all.

Mixed Anhydrides in the Ketene–Aldehyde Reaction Products.—The reactions just described were applied on the brown, viscous products of the reaction between ketene, aldehydes and potassium acetate. (a) Vacuum distillation of the reaction product from ketene and benzaldehyde produced some crystalline cinnamic anhydride. The corresponding product from *m*-nitrobenzaldehyde gradually deposited crystals of m-nitrocinnamic anhydride on standing. (b) When phosphorus trichloride was mixed with the benzaldehyde–ketene product, the yield of acetyl chloride indicated **50%** of acetic cinnamic anhydride in the material. (c) Using the oxalic acid and pyridine method of analysis there was found 59% of furylacrylic acetic anhydride and 30% of cinnamic acetic anhydride, respectively. The amounts of furylacrylic and cinnamic acids isolated agreed with these values.

Mechanism of the Reaction.—If one assumes that a molecule each of ketene and aldehyde participate in the first stage of the reaction, there are three modes of addition to be considered:



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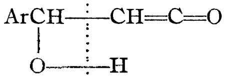
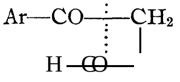


II



III

Formula (I) represents a *β*-lactone. This is undoubtedly formed but whether it is formed directly or by isomerization of (II) is debatable. Formula (II) represents an hydroxyketene, a new type of compound which might isomerize into (I) and concurrently might form an acetic ester with an excess of ketene. In this ester, the acetate radical is at an end of a "three carbon system," with an aryl group at the same end. Hence, a

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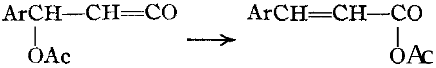
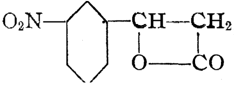
(8) Besson, *Compt. rend.*, 125, 771 (1897).

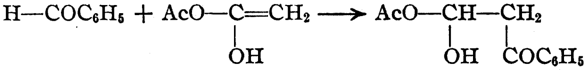
rearrangement[9] typical of such systems would be anticipated. The resultant compound would be the mixed anhydride



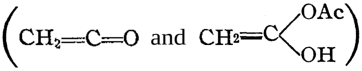
$$\underset{\displaystyle\text{OAc}}{\text{ArCH}}\text{—CH=CO} \longrightarrow \text{ArCH=CH—}\underset{\displaystyle\text{OAc}}{\text{CO}}$$

The β-lactone provides a satisfactory explanation for the arylethylenes which were isolated and the hydroxyketene for the mixed anhydrides. It would be conceivable to consider the 8-lactones as forerunners of the mixed anhydrides if they could rearrange into unsaturated acids. These acids add ketene normally and give mixed anhydrides. However, β-lactones do not undergo rearrangement by heat to unsaturated acids. They give unsaturated hydrocarbons and carbon dioxide instead. Furthermore, the β-lactone, , is stated[4] to be stable at the temperatures used. Hence if formed it should not have decomposed into *m*-nitrocinnamic acid, yet m-nitrocinnamic acetic anhydride was formed.

Formula (III) lacks support in the present work since benzoylacetaldehyde was not found and since it cannot be regarded as a probable intermediate in the production of either the arylethylenes or the mixed anhydrides. Mention is made of formula (111), however, because of its bearing on Kalnin's recently proposed mechanism[10] for the Perkin reaction. Kalnin assumed the first step to be enolization of acetic anhydride by potassium acetate. Then he postulated addition of benzaldehyde to it with scission of the aldehyde into hydrogen and benzoyl



$$\text{H—COC}_6\text{H}_5 + \text{AcO—}\underset{\displaystyle\text{OH}}{\text{C}}\text{=CH}_2 \longrightarrow \text{AcO—}\underset{\displaystyle\text{OH}}{\text{CH}}\text{—}\underset{\displaystyle\text{COC}_6\text{H}_5}{\text{CH}_2}$$

Because of the structural similarity of ketene to enolized acetic anhydride  $\left(\text{CH}_2\text{=C=O and CH}_2\text{=C}\begin{matrix}\text{OAc}\\ \text{OH}\end{matrix}\right)$ it is reasonable to think that benzaldehyde should add to ketene analogously and produce benzoylacetaldehyde, were this equation correct. However, as stated above, this was not found. Furthermore, with this mechanism it is not apparent why potassium acetate is necessary in the ketene–benzaldehyde reaction, for C=C exists in ketene (whereas it does not in acetic anhydride).

Other objections to Kalnin's mechanism are these. Phthalic anhydride[11] or benzoyl cyanide,[12] with no labile hydrogen, may replace benzaldehyde in the reaction with acetic anhydride and potassium acetate. Also, the fact

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[9] Burton and Ingold, *J. Chem. Soc.*, 906 (1928); Burton, *ibid.*, 1650 (1928); 248 (1930): 759 (1931). The wandering of not only the acetate radical but also others such as chloride, bromide, trichloroacetate and *p*-nitrobenzoate is shown and the influence of aryl groups in facilitating the change of ArCHXCH=CH_2 to ArCH=$CHCH_2X$ is demonstrated.

[10] Kalnin, *Helv. Chim. Acta*, 11, 977 (1928).

[11] Michael and Gabriel, *Ber.*, 10, 391 (1877): Gabriel and Michael, *ibid.*, 11, 1007 (1878).

[12] Mueller, Ann., 491, 251 (1931).

that bases induce the condensation of methyl benzoylformate, which contains no labile hydrogen, with methyl cyanacetate[13] is a similar objection.

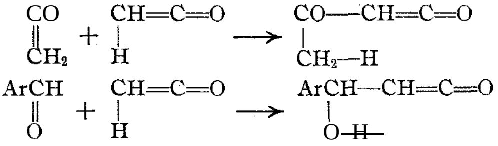
The most satisfactory interpretation of the Perkin reaction is one originally suggested by Michael,[14] which aligns it with well-known condensations of aromatic aldehydes with other aldehydes, ketones and esters, all of which are catalyzed by a base. The general equation becomes

$$\mathrm{ArCHO + RCH_2{-}CO{-}Z \xrightarrow{base} Ar{-}CHOH{-}CHR{-}CO{-}Z}$$

wherein Z represents H, R, OR or OCOR. Whether or not dehydration to $\mathrm{ArCH{=}CR{-}CO{-}Z}$ occurs depends on the conditions of the reaction. In such a process, the base may be considered to loosen the C—H bond in $\mathrm{RCH_2{-}CO{-}Z}$. Two carbonyl groups are present to compete for the hydrogen, namely, the one in benzaldehyde and the one in acetic anhydride. The former gives rise to the Perkin reaction (irreversible) and the latter to enolized acetic anhydride (reversible). With this viewpoint, the double bond of enolized acetic anhydride loses the significance ascribed to it by Kalnin.

A strictly analogous mechanism best pictures the formation of the hydroxyketene (II) in the ketene–aldehyde reaction.

Finally, it is interesting to call attention to the polymerization of ketene. If the dimer of ketene is regarded as acetylketene, $\mathrm{CH_3COCH{=}C{=}O}$, rather than cyclobutanedione, a preference which seems necessary to account for its polymerization[15] into dehydroacetic acid, then the mechanism for the addition of ketene to itself resembles that of its addition to aldehydes



$$\begin{array}{l}\mathrm{CO}\\ \|\\ \mathrm{CH_2}\end{array} + \begin{array}{l}\mathrm{CH{=}C{=}O}\\ |\\ \mathrm{H}\end{array} \longrightarrow \begin{array}{l}\mathrm{CO{-}CH{=}C{=}O}\\ |\\ \mathrm{CH_2{-}H}\end{array}$$

$$\begin{array}{l}\mathrm{ArCH}\\ \|\\ \mathrm{O}\end{array} + \begin{array}{l}\mathrm{CH{=}C{=}O}\\ |\\ \mathrm{H}\end{array} \longrightarrow \begin{array}{l}\mathrm{ArCH{-}CH{=}C{=}O}\\ |\\ \mathrm{O{-}H}\end{array}$$

Experimental Part

Ketene was synthesized from acetone by pyrolysis.[16] In experiments where it was desired to have the ketene completely free from acetone vapor, the latter was removed by passing the gases through a −80° condenser.

Acetyl Chloride from Acetic Anhydride and Phosphorus Trichloride.—Twenty cc. (21.6 g.) of acetic anhydride and 20 cc. (32.3 g.) of phosphorus trichloride were distilled together with a good column. The acetyl chloride which formed distilled between 51–52°. The yield was 29.5 g. or 89% of the calculated amount. The residue was a yellow, paraffin-like solid.[8]

Mixed Anhydrides from Ketene

Furylacrylic Acetic Anhydride.—Fifteen grams of furylacrylic acid was suspended in 50 cc. of dry, ice-cold ether and ketene was passed in until it was no longer absorbed.

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(13) Kohler and Corson, THIS JOURNAL, 45, 1975 (1923).

(14) Michael, Ber., 34, 918 (1901).

(15) Hurd, Sweet and Thomas, THIS JOURNAL, 55, 335 (1933).

(16) Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1924, Vol. IV, p. 40.

The ether was then evaporated *in vacuo*. The product was a slightly brown liquid which possessed a sharp odor. On standing it gradually changed into a black jelly, a change which was facilitated by heating. The compound (freshly prepared) was analyzed[5] with dry oxalic acid and pyridine.

Anal. Anhydride calcd. for $C_9H_8O_4$, 100%. Found: anhydride, 99.5%.

Cinnamic Acetic Anhydride.—Just as in the previous case, 15 g. of cinnamic acid was suspended in 50 cc. of cold, dry ether and treated with ketene. The residue on evaporation of the ether was a slightly colored liquid with a sharp odor.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.26. Found: C, 69.1; H, 5.22.

On standing at room temperature, cinnamic acetic anhydride slowly deposited cinnamic anhydride.[17] This action was rapid on heating.

Ten grams of cinnamic acetic anhydride was distilled with 11 g. of phosphorus trichloride. There was formed 3.5 g. (84.5%) of acetyl chloride, b. p. 52°, which gave acetanilide, m. p. 114°, on reaction with aniline.

Cinnamic Anhydride.—Cinnamic anhydride, prepared by pyrolysis of the acetic cinnamic anhydride and recrystallized from xylene, melted at 134°. It was found to distil practically unchanged at 23 mm. at a bath temperature of 270°. Search was made for styrene as a decomposition product without success.

When pure cinnamic anhydride was analyzed by the oxalic acid and pyridine method the reaction was not quantitative. Thus, in one experiment 0.2778 g. of anhydride gave rise to 40.2 cc. (corr.) of gas which represents a conversion of 89.5%. In three similar runs the values were 87.0, 88.8 and 91.1%. Since the purity of the cinnamic anhydride was not in question, the method evidently is not a quantitative one in this case.

Reaction of Aldehydes with Ketene and Potassium Acetate

Ketene–Furfural Reaction Product.—Fifty cc. (58 g. or 0.6 mole) of furfural and 3.3 g. of freshly fused potassium acetate were placed in a flask and 0.8 mole of ketene passed in. The furfural warmed up to about 60° and turned dark rapidly. It required about three hours to generate this amount of ketene and the furfural was quite warm until the last half hour of the reaction. The total increase in weight was 27 g. and the product was a thick, dark brown liquid having an odor of furfural. It was analyzed for its acetic furylacrylic anhydride content by the oxalic acid and pyridine method. A molecular weight determination was also made on this material.

Anal. Subs. 0.4358: cc. of gas (corr.), 64.3. Anhydride content calcd. as $C_4H_3OCH{=}CHCOOCOCH_3$, 59.3%. *Mol. wt.* Subs. 0.3883. Solvent (benzene), 21.9. Freezing point lowering, 0.505". Mol. wt. calcd. for $C_9H_8O_4$, 180; found, 175.

Conversion into Furylethylene

(a) Direct Heating.—Some of the tarry reaction product was heated in a small distillation flask. The liquid distillate was collected in a test-tube which contained a trace of pyrogallol to prevent polymerization. This distillate possessed the properties of furylethylene.3 It was a liquid insoluble in water. It boiled at 100°. It polymerized and turned dark colored on standing and it decolorized potassium permanganate solution instantly.

(b) Steam Distillation.—Steam was passed into the reaction mixture of a new run starting again with 50 cc. of furfural. The non-aqueous layer of the distillate was the top layer. Its volume was 32 cc. It was separated and dried over calcium chloride. In these and in subsequent manipulations, a trace of pyrogallol was always present. When dry, 16.5 cc. was collected by distillation to 110°. The remaining 10.5 cc, was largely furfural. After washing the 16.5 cc. to remove acetone, about 9.5 cc. of liquid

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(17) Compare Autenrieth, Ber., *34*, 186 (1901).

remained which was very unsaturated toward permanganate solution and bromine water. After drying and distilling all boiled at 97° or below showing it to be chiefly furylethylene.

The residue from which the furfural and furylethylene had been steam distilled was made alkaline with aqueous sodium hydroxide. Four grams of a black tar remained undissolved. The yield of furylacrylic acid (m. p. 139°) which separated by adding acid to the alkaline solution was 36 g. This 36 g., coming from 58 g. of furfural, is a 43.5% yield. From the furylacrylic acetic anhydride content (59.3%) of the crude reaction product which weighed 85 g., it would have been possible to obtain 38.6 g. of furylacrylic acid. The value of 36 g., therefore, is confirmatory evidence that the mixed anhydride was present in the amount indicated.

Ketene–Benzaldehyde Reaction Product.—Fifty cc. (53 g. or 0.5 mole) of benzaldehyde which had been freshly distilled and 3 g. of fused potassium acetate were treated with ketene until there was no further action as evidenced by a heating effect (tested by feeling with the hand). During most of the time the ketene was being added the reaction mass maintained itself at a temperature of about 60°. The gain in weight of the reaction flask was 26 g. which, if caused entirely by addition of ketene, represents 0.62 mole. The product was a thick, brown liquid having the odor of benzaldehyde as well as a slight ester odor. Actually, its benzaldehyde content was at least 14% since from one gram of the crude substance there was produced 0.25 g. of benzaldehyde phenylhydrazone. The crude material was analyzed for its acetic cinnamic anhydride content with anhydrous oxalic acid and pyridine. Also, its apparent molecular weight was determined.

Anal. Subs., 1.0437, 1.0712; cc. of gas (corr.), 75.4, 76.4. Anhydride content calcd as $C_6H_5CH{=}CHCOOCOCH_3$, 30.6, 30.2 Mol. wt. Subs. 0.7847; g. of solvent (benzene), 30.7; depression of freezing point, 0.745°. Calcd. for $C_{11}H_{10}O_3$, mol. wt., 190; found, 172.

By steam distilling the ketene–benzaldehyde product from one run as above the excess of benzaldehyde was removed. The residue was extracted with alkali and the extract acidified to precipitate the cinnamic acid, m. p. 126°. Sixteen grams of it was isolated, which is a 21.8% yield based on the original benzaldehyde. Since the cinnamic acetic anhydride content of the crude reaction mixture which weighed 79 g. was 30.6%, the weight of cinnamic acid which this should create is 18.8 g. The 16 g. which was isolated is satisfactory agreement.

The product from another identical run was vacuum distilled at 6 mm. Between 40–55°, 25 cc. of benzaldehyde which was admixed with a little styrene distilled. From 55–170°, there was collected 5 cc. of styrene which contained a little benzaldehyde. From 170–174°, a light yellow solid distilled (5 g.) which was colorless when purified. It melted at 129° and was shown to be cinnamic anhydride. The styrene was identified by converting it into the dibromide which melted at 61°.

Five grams of the ketene–benzaldehyde product was distilled with 5 g. of phosphorus trichloride and the liquid boiling up to 85° was collected. On redistillation, 0.5 cc. of liquid was collected up to 65°. Assuming a quantitative reaction, this yield of acetyl chloride would require 2.4 g. of acetic cinnamic anhydride. When treated with aniline, this acetyl chloride gave acetanilide, m. p. 114°.

m-Nitrobenzaldehyde and Ketene.—Fifty grams of m-nitrobenzaldehyde was suspended in 100 cc. of benzene and a little fused potassium acetate added. Ketene was then passed in till there was no longer a heating effect. This aldehyde gradually went into solution and the solution turned dark brown Toward the end of the reaction an almost black oil separated on the bottom of the flask. After standing for several days, this black oil changed into a light yellow solid. This solid was filtered off and washed with benzene; yield, 15.5 g. or 25%. It melted at 206". Its insolubility in 5% potassium hydroxide combined with the fact that a mired melting point value of 180° was obtained with known m-nitrocinnamic acid demonstrated that it was not *m*-nitrocinnamic acid. When some of the solid was boiled with 5% potassium hydroxide solution it slowly dissolved Acidification of this solution gave m-nitrocinnamic acid melting at 196°. The melting point of known m-nitrocinnamic acid was not lowered by mixing with this acid. Thus, the original substance was a hydrolyzable derivative of m-nitrocinnamic acid.

m-Nitrocinnamic Anhydride.—This compound has not been described in the literature. Elemental analyses cannot be used to identify it since the percentages are so nearly identical to the values with the free acid. A molecular weight determination and an equivalent weight titration were used to prove that the 206° compound was m-nitrocinnamic anhydride. The former was determined by Pastak's method[18] using trinitrotoluene as solvent.

Mol. wt. Subs. 0.2443, 0.5269; g. of solvent (TNT), 12.569, 12.790. Depression of freezing point, 0.65°, 1.3". Calcd. for $C_{18}H_{12}O_7N_2$, mol. wt., 368; found, 344, 364. ($K = 11.5°$/mole/1000 g. of solvent.) *Equiv. wt.* Subs. 0.1123 g. dissolved in 5.00 cc. of alc. KOH (5 cc. ≈ 25.88 cc. of 0.2016 *N* HCI); cc. 0.2016 *N* HCl, 22.95. Calcd. for $C_{18}H_{12}O_7N_2$, equiv. wt.. 184; found, 190.

The benzene filtrate from which the 15.5 g. of m-nitrocinnamic anhydride precipitated was evaporated. The residue was a thick brown liquid. It reacted with concd. alcoholic potash so vigorously as to make the alcohol boil. However, the reaction was quite slow when 20 g. of it was treated at 0° with a solution of 10 g. of potassium hydroxide in 250 cc. of alcohol. After standing overnight the solution was evaporated on the steam-bath. No success attended efforts to extract the tar with ether or benzene. On adding water a brown solution formed but most of the tar remained behind. The solution was decolorized with charcoal and acidified. Three grams of m-nitrocinnamic acid separated; m. p. 193° and mixed m. p. 195°. This is a 15% yield.

The original *m-nitrobenzaldehyde–ketene* product does not contain acid since on standing for one week with sodium carbonate solution there was no brown color in the aqueous layer and there was no evidence of gas being evolved at any time.

Twenty grams of the m-nitrobenzaldehyde–ketene product was heated by an open, moving flame in an evacuated apparatus. Before there was any profound decomposition, 3.5 g. of a liquid was collected as a distillate. This liquid was thought to contain m-nitrostyrene for it decolorized potassium permanganate solution readily, it absorbed bromine instantly and its odor was similar to that of styrene. It froze at a temperature below −20°, whereas m-nitrostyrene is stated to freeze at −15° and to melt at −5°. Although the liquid absorbed bromine it was not possible to isolate any *m*-nitrostyrene dibromide from the reaction mixture. Hence, it cannot be stated definitely whether or not m-nitrostyrene was formed, but its presence is strongly indicated.

Synthesis of *m*-Nitrocinnamic Anhydride.—One gram of m-nitrocinnamic acid was refluxed with 3 cc. of acetic anhydride for five minutes. White crystals separated on cooling. These were washed with benzene and then with ether; yield, 0.3 g.; m. p. 206° A mixed melting point with the product obtained by the action of ketene gave 204°. m-Nitrocinnamic anhydride did not react with a mixture of dry oxalic acid and pyridine.

The anhydride was further identified by converting it into the methyl ester. One gram of the anhydride was refluxed for four hours with 10 cc. of methanol, the insoluble part filtered off, and the filtrate diluted with water. Methyl m-nitrocinnamate separated as small, slightly colored crystals. With no further purification, it melted at 118° as compared with the literature value[19] of 124".

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(18) Pastak, Bull. *soc. chim.*, *39*, 82 (1926).

(19) *Sudborough* and *Lloyd, J. Chem. Soc.*, **73**, 85 (1898).

By warming 7 g. of m-nitrocinnamic anhydride with 5 cc. of aniline, *m*-nitrocinnamanilide was prepared. The solid was washed with dilute alkali and then with dilute acid. After recrystallization from benzene the needle crystals melted at 194–195°.

Summary

In the presence of a little potassium acetate, ketene reacts exothermically with aromatic aldehydes (benzaldehyde, furfural, *m*-nitrobenzaldehyde). The primary product was considered to be a non-isolable hydroxyketene, Ar—CHOH—CH=C=O, but the chief product isolated was a mixed acetic anhydride, $ArCH{=}CH{-}CO{-}O{-}COCH_3$. The presence of a @-lactone was indicated in lesser amounts inasmuch as moderate heating of the reaction product gave rise to arylethylenes, $ArCH{=}CH_2$. The mechanism for the production of these substances is given. The similarity of this reaction to the Perkin reaction is pointed out and the mechanism for the latter reaction discussed. In this connection, some serious objections to Kalnin's mechanism are raised.

Acetic cinnamic anhydride and acetic furylacrylic anhydride were synthesized by the reaction of ketene and cinnamic acid or furylacrylic acid. These mixed anhydrides undergo pyrolysis into the symmetrical anhydrides. Also, they give good yields of acetyl chloride with phosphorus trichloride and they react quantitatively with dry oxalic acid and pyridine, each mole of mixed anhydride giving rise to a mole each of carbon monoxide and carbon dioxide. Cinnamic anhydride reacts with oxalic acid and pyridine, but not quantitatively.

m-Nitrocinnamic anhydride was synthesized and studied.

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The Rearrangement of Alkenyl Phenyl and Cresyl Ethers and the Syntheses of Isopropenyl Phenols and their Reduction Products[1]

By JOSEPH B. NIEDERL AND EDWARD A. STORCH

Theoretical Part

In previous publications report was given on the successful rearrangement of saturated alkyl phenyl ethers[2] brought about chiefly by the action of an acetic–sulfuric acid mixture. That the chemical nature of the catalyzer does not play any integral part in these molecular migrations had been shown[3] and has been further verified recently by Sowa, Hinton and Nieuwland,[4] who checked the experimental findings of this Laboratory in the synthesis of thymol and its isomers from the corresponding isopropyl phenyl ethers. The purpose of the research presented in this communication was to extend these studies in molecular rearrangements to short-chain, alkenyl phenyl ethers (isopropenyl phenyl and cresyl ethers) in order to establish the limitations, general applicability, rules of migration, and, in general, to obtain a better theoretical understanding of this phenomenon. The latter object gains in interest, especially in view of the present-day conceptions of the reaction mechanism involved in such molecular transitions. As will be shown later, the accomplished rearrangement of the various isopropenyl phenyl ethers, as set forth herein, makes a rigid application of some of the present-day theories quite difficult. Therefore, in the following, attempts have been made to harmonize and to bridge various gaps between such accepted theories and the new experimental findings by broadening the scope of the former and incorporating certain physico-chemical energy principles.

Any such attempts, however, required first of all the determination of the structure and especially the position taken up by the migrating group in the benzene nucleus.

The isopropenyl phenyl and cresyl ethers mentioned above were prepared by treating isopropenyl bromide with the appropriate potassium phenolate. The rearrangement of the ethers was carried out by refluxing with a 10% solution by volume of sulfuric in glacial acetic acid.

Ortho Rearrangement.—The first point of attack was isopropenyl

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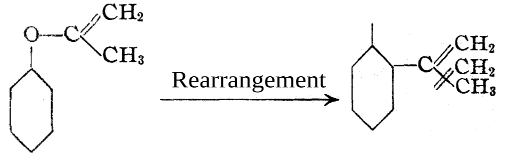
[1] From Part I of the thesis presented by Edward A. Storch to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

[2] Niederl and Natelson, THIS JOURNAL, 53, 272, 1928 (1931); 54, 1063 (1932).

[3] Rheinische Kampfer-Fabrik, Swiss Patent 144,207 (1931); Schoeller, U. S. Patent 1,835,344 (1931).

[4] Sowa, Hinton and Nieuwland, THIS JOURNAL, 54, 2019 (1932).

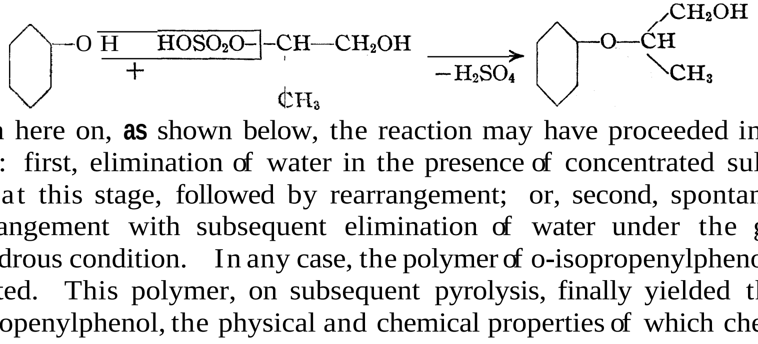
phenyl ether. Its rearrangement gave rise to a product, the main portion of which was identified as *o*-isopropenylphenol.[5] It yielded upon catalytic reduction *o*-isopropylphenol,[6] which was identified as *o*-isopropylphenoxyacetic acid.[7] The original isopropenylphenol yielded a crystalline hexabromo derivative which was different from the corresponding bromine derivative of *p*-isopropenylphenol, reported in the literature.[8] The above evidence suggests that ortho migration was favored and that the final product was o-isopropenylphenol.



This same product: was resynthesized from allyl alcohol and phenol in the presence of concentrated sulfuric acid in the cold. A polymer was obtained which on distillation gave o-isopropenylphenol, and the following mechanism explaining its formation has been shown to be a general one for addition of phenols to an ethylenic linkage, with sulfuric acid as the condensing agent.[9] The first step involved the addition of sulfuric acid to allyl alcohol with the formation of a-ally101 sulfate

$$CH_2{=}CHCH_2OH + H_2SO_4 \longrightarrow CH_3CH(CH_2OH)OSO_2OH$$

In the next step ether formation can be assumed to take place[10] with the formation of β-phenoxypropylene glycol



From here on, as shown below, the reaction may have proceeded in two ways: first, elimination of water in the presence of concentrated sulfuric acid at this stage, followed by rearrangement; or, second, spontaneous rearrangement with subsequent elimination of water under the given anhydrous condition. In any case, the polymer of o-isopropenylphenol was isolated. This polymer, on subsequent pyrolysis, finally yielded the *o*-isopropenylphenol, the physical and chemical properties of which checked with the material obtained upon the rearrangement of the isomeric ether and with the constants given in the literature.

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[5] (a) Béhal and Tiffeneau, Bull. *soc. chim.,* [4] 3, 315 (1908); (b) Hoering and Baum, German Patent 208,886 (1909); (c) Fries and Volk, *Ann.,* 379, 95 (1911).

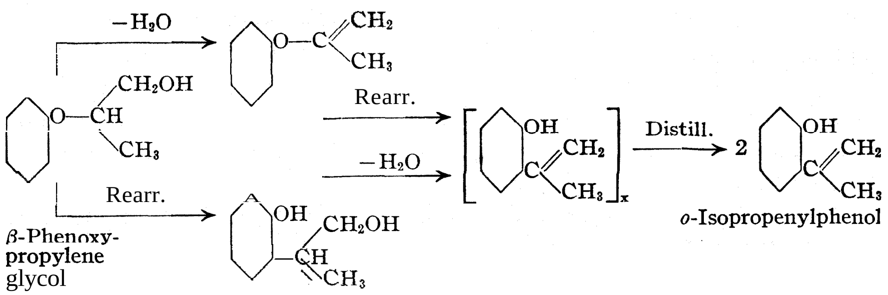
[6] (a) Spica, *Gazz. chim. ital.,* 9, 42 (1879); *Jahvesb.,* 663 (1880); (b) Niederl and Natelson, THIS JOURNAL, 53, 1933 (1931).

[7] Fileti, *Gazz. chim. ital.,* 16, 129 (1886).

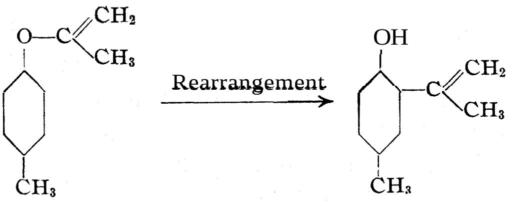
[8] Zincke and Greuters, *Ann.,* 343, 94 (1905).

[9] Smith and Niederl, THIS JOURNAL, 53, 806 (1931); Niederl, Smith and McGreal, *ibid.,* 53, 3390 (1931).

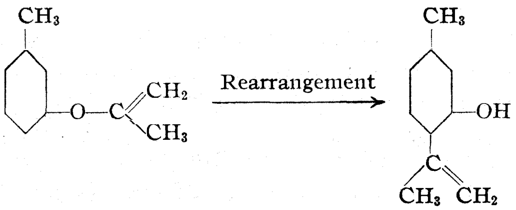
[10] Niederl and Natelson, *ibid.,* 53, 273 (1931).



In the rearrangement of isopropenyl *p*-cresyl ether, the isopropenyl group could migrate to the ortho position only, the para position being occupied and meta rearrangement being unusual. The properties of the resulting product, 1-hydroxy-4-methyl-2-isopropenylbenzene, were in agreement with the literature.[11] As before, the same product was prepared from allyl alcohol and *p*-cresol in the presence of sulfuric acid. The compound obtained was identical with the one mentioned above and its formation by rearrangement may be represented as follows



The rearrangement of the isopropenyl m-cresyl ether resulted in a phenol which corresponded with the 3-hydroxy-1-methyl-4-isopropenylbenzene known in the literature.[11] The product obtained by the condensation of allyl alcohol and *m*-cresol was identical with the above. The phenol yielded a bromine derivative corresponding with the pentabromodehydrothymol (2,5,6,4^2,4^2-pentabromo-3-hydroxy-1-methyl-4-isopropenylbenzene) reported in the literature.[12] This evidence would tend to indicate that the isopropenyl group migrated to the ortho position.



This product was reduced catalytically first to thymol and further to a menthol.

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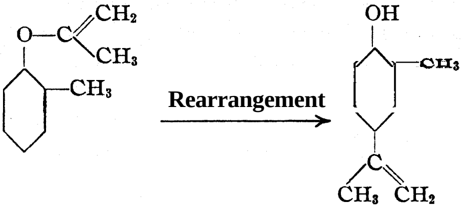
[11] (a) Fries and Fickewirth, Ann., 362, 46 (1908); (b) Guillaumin, Bull. soc. chim., [4] 7, 381 (1910).

[12] Baeyer and Seuffert, Ber., 34, 47 (1901).

It may be mentioned that in the case of the condensation of o-cresol and allyl alcohol an alkali-insoluble higher boiling liquid was obtained in small amounts as a by-product. The formation of such a compound is open to several interpretations, included among which are a dehydration reaction or possibly migration into the side chain ortho to the hydroxyl group[13] followed by ring closure.

Para Rearrangement.—The rearrangement of the isopropenyl *o*-cresyl ether yielded chiefly a product which proved to be the 1-hydroxy-2-methyl-4-isopropenylbenzene. A product obtained on condensing allyl alcohol with o-cresol was identical with it. As mentioned above, along with this main product in each case was isolated a small quantity of higher boiling, alkali-insoluble liquid.

Inasmuch as all the foregoing reactions showed the isopropenyl residue migrating in an ortho position to the hydroxyl group, the above case seems to show a peculiarity in that para rearrangement is favored.



Furthermore, this case is worthy of careful study since Hurd[14] states, "If either one of the ortho atoms of the aromatic nucleus is unsubstituted, the allyl group almost invariably migrates into the ortho position; if both, however, are substituted, para rearrangement occurs."

There have been cases recorded where although one or even both ortho positions were vacant, para rearrangement ensued.[3,4,15]

In attempting to establish the structure, the product obtained by the rearrangement of isopropenyl o-cresyl ether was reduced catalytically and the crude material on distillation at ordinary pressure yielded a colorless liquid the characteristics of which were in close agreement with 1-hydroxy-2-methyl-4-isopropylbenzene.[16]

On bromination of this reduced product and recrystallization of the reaction material from alcohol, there was isolated a crop of very characteristic lustrous, golden-yellow plates which resembled in physical appearance those described in the literature.[17] However, on continued purification

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[13] Van Alphen, *Rec. trav. chim.*, *46*, 287 (1927).

[14] Hurd, p. 214, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., New York, 1929.

[15] (a) Van Alphen, *Rec. trav. chim.*, *46*, *288*, 799 (1927); (b) Niederl and Natelson. THIS JOURNAL, 53, 1931 (1931).

[16] (a) Kelbe, Ann., 210, 40 (1881); (b) Spica, *Gazz. chim. ital.*, *12*, 552 (1882).

[17] Jesurun, *Ber.*, 19, 1414 (1886).

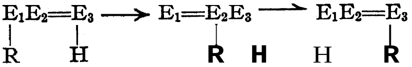
this product not only showed a higher melting point, but also analysis proved it to be a tetrabromo derivative.

The 1-hydroxy-2-methyl-4-isopropenylbenzene was itself further characterized by an acetic acid and a pentabromo derivative.

In conclusion, on the basis of the work done so far with the isopropyl, vinyl, and isopropenyl phenyl and cresyl ethers and the corresponding phenols, it appears that migration of the alkyl or alkenyl side chain ortho to the hydroxyl group is favored, except where one or both of the ortho positions are already occupied or are influenced by steric hindrance, then para rearrangement predominates.

As was previously stated, in view of these advances in the rearrangement of alkyl and alkenyl ethers a satisfactory reaction mechanism that would be in harmony with these experimental findings should be sought. Evidently, Claisen's mechanism[18] for the rearrangement of unsaturated alkyl phenyl ethers, in which the migration is claimed to take place through the gamma carbon atom, cannot be applied to the cases cited here due to the absence of the required atomic grouping. Hurd and Cohen's[19] suggestion of free radical formation would require the production of certain by-products, that so far could not be found, while Kursanov's[20] hypothesis of scission of the ether into an alkali halide and recombination with a nuclear carbon atom in the manner of the Friedel–Crafts reaction[21] is *a priori* out of the question for the cases cited. In consideration of the rearrangement mechanism offered by Van Alphen,[13] involving oxonium compound formation and the one advanced by Lapworth[22] for various other types of molecular rearrangements and already applied in the synthesis of thymol, its derivatives and homologs,[22a] the following reaction mechanism is herewith offered.

As the following arrangement of atomic groupings appears to be fundamental for the migration of the alkyl radical to the nuclear carbon atom ortho to the ether oxygen



$$\underset{R}{E_1}E_2{=}\underset{H}{E_3} \longrightarrow E_1{=}\underset{R}{E_2}E_3 \;\; H \longrightarrow \;\; H \;\; E_1E_2{=}\underset{R}{E_3}$$

it must be applicable to the cases presented herein. Where ortho rearrangement takes place, namely, isopropenyl phenyl, m-cresyl and #-cresyl ethers, the following reaction mechanism could be given. It should be noted that these ethers possess two of the active atomic groupings.

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[18] Claisen, *Ber.*, 45, 3157 (1912); *Ann.*, 237, 261 (1887); 401, 21 (1914); 418, 69 (1919); *Z. angew. Chem.*, 36, 478 (1923); Claisen and Tietze, *Ber.*, 58, 275 (1925); 59, 2344 (1926).

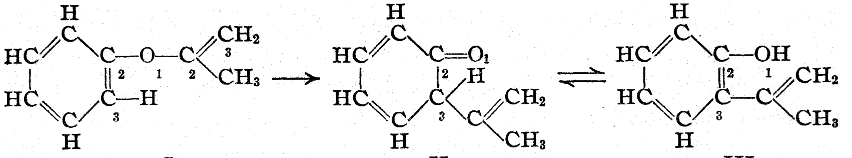
[19] Hurd and Cohen, THIS JOURNAL, 53, 1917 (1931).

[20] Kursanov, J. Russ. *Phys.-Chem. Soc.*, 48, 1172 (1914).

[21] Friedel and Crafts, *Ann. chim. phys.*, [6] *1*, 502 (1884).

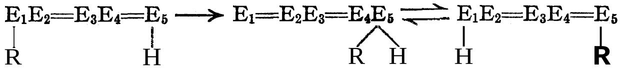
[22] Lapworth, J. *Chem. Soc.*, 73, 445 (1898).

[22a] Niederl and Natelson, THIS JOURNAL, 54, 1063 (1932).



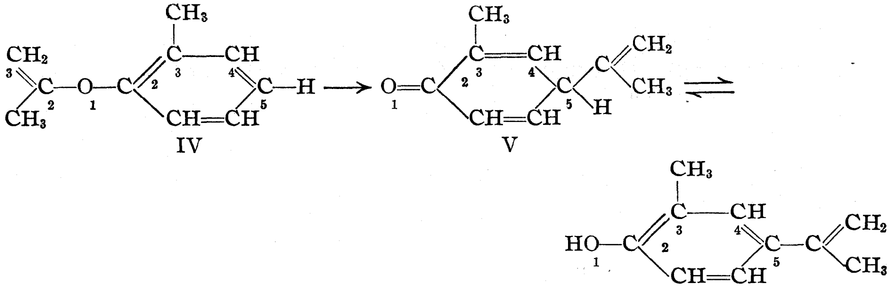
I II III

The original Lapworth theory must be extended to explain the formation of a para isomer.



$$\underset{R}{E_1}E_2{=}E_3\underset{H}{E_4}{=}E_5 \longrightarrow E_1{=}E_2E_3{=}\underset{R\ H}{E_4}E_5 \rightleftharpoons \underset{H}{E_1}E_2{=}E_3E_4{=}\underset{R}{E_5}$$

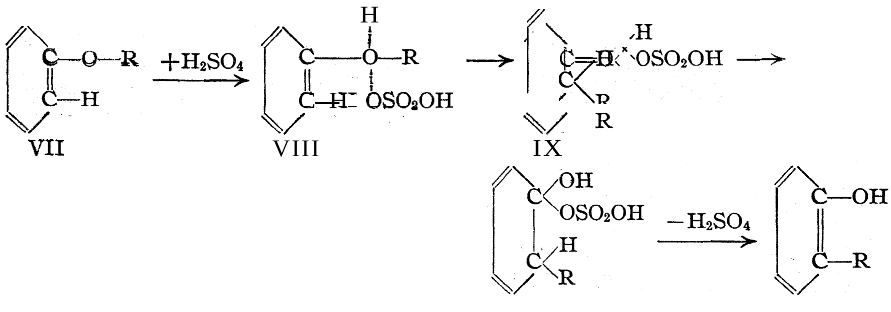
Applied to the case of the observed formation of the para isomer of isopropenyl o-cresol, the intramolecular rearrangement can then be illustrated in the following manner.



IV V VI

Quite obviously, the ether does not pass to the quinoid form (II) without some impulse; nor is it expected that the ether changes directly to the phenol, in spite of the fact that the phenol has a lower energy potential than the ether.. It is assumed therefore that the ether first passes to the intermediate structure II, at a higher energy level, from which it now readily goes to the phenol III, at the lowest energy level.

The impulse for the change from the ether to the intermediate compound is postulated as arising directly from an addition of sulfuric acid to the ether oxygen, forming a transitory phenyl isopropenyl oxonium sulfate (VIII) with a higher energy potential.



VII VIII IX

Related oxonium sulfates of ethers are known in the literature.[23]

The oxonium compound then passes to the more stable quinoid configuration (IX—similar to II). These quinoid addition compounds have been reported by Richter.[24]

The next step in the mechanism involves a change from the quinoid carbonyl addition compound to a still more stable one of a hemi-acetal structure (X). Hydrolysis with the elimination of sulfuric acid is brought about resulting in the final phenolic product (XI).

An effective rationalization of the suggested mechanism may be attained from a consideration of the repulsion energies of the atomic kernels in the bonds involved. The following scheme represents the changes in the bonds during the rearrangement.

$$\underbrace{(\mathrm{O—C}) + (\mathrm{C—H})}_{\text{VII. Ether}} \longrightarrow \underbrace{(\mathrm{O—C}) + (\mathrm{O—H}) + (\mathrm{O—O}) + (\mathrm{C—H})}_{\text{VIII. Ether oxonium compound}} \longrightarrow$$

$$\underbrace{(\mathrm{O—H}) + (\mathrm{O—O}) + (\mathrm{C—H}) + (\mathrm{C—C})}_{\text{IX. Quinoid carbonyl addition compound}} \longrightarrow \underbrace{(\mathrm{O—H}) + (\mathrm{O—C}) + (\mathrm{C—H}) + (\mathrm{C—C})}_{\text{X. Quinoid hemi-acetal}} \longrightarrow$$

$$\longrightarrow \underbrace{(\mathrm{O—H}) + (\mathrm{C—C})}_{\text{XI. Phenol}}$$

According to Latimer[25] the values of the repulsion energies expressed in kilocalories, in the above linkages are

(C—H)	550 kilocal.	(O—C)	2800 kilocal.
(O—H)	940 kilocal.	(O—O)	4550 kilocal.
(C—C)	1700 kilocal.		

Substituting these values in the above equation

$$\underset{\text{VII}}{3350} \xrightarrow[+5490]{} \underset{\text{VIII}}{8840} \xrightarrow[-1150]{} \underset{\text{IX}}{7690} \xrightarrow[-1700]{} \underset{\text{X}}{5590} \xrightarrow[-3350]{} \underset{\text{XI}}{2640}$$

It can now be seen that to pass from the ether (VII) to the oxonium compound (VIII) involves a gain of repulsion energy amounting to 5490 kilocalories, which appears to furnish the necessary impulse for the following changes. All the succeeding intramolecular rearrangements are accompanied by losses of repulsion energy amounting to 1150, 1760 and 3350 kilocalories, respectively, until the more stable phenol with the least intramolecular energy content is obtained.

This mechanism is not specific for a rearranging mixture of sulfuric and glacial acetic acids. Where boron trifluoride[4] or other substances have been used, the reaction mechanism may be postulated as being quite similar except that an addition of boron trifluoride takes place instead of sulfuric acid to form the transitory oxonium compound.

Furthermore, in isolated cases (allyl, cinnamyl and diisobutyl phenyl

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[23] Erlenmeyer and Kirchbaumer, Ber., 7, 699 (1874); Tschelinzew and Koslow, *J. Russ. Phys.-Chem. Soc.*, 46, 711 (1915).

[24] Richter, Ber., 43, 3600 (1910).

[25] Latimer, THIS JOURNAL, 51, 4168 (1929).

ethers) where heat alone has been employed to effect rearrangement, the above mechanism offers a satisfactory explanation. Assuming the formation of oxonium compounds between identical molecules, then the succeeding transitory bimolecular addition compounds of the quinhydrone type may be formed and finally the substituted phenol is obtained.

In regard to the velocity of reaction in the rearrangement of alkyl and alkenyl phenyl ethers, work in this Laboratory with vinyl, isopropyl, isopropenyl, secondary-butyl and -amyl and diisobutyl phenyl ethers tends to indicate that the longer the wandering side chain (greater the molecule), the more rapid is the migration. On the basis of physical principles such a tendency may be explained as being due to the greater possibility of collision with larger molecules proceeding through the changes indicated by the above mechanism ("Zweistoss" system).

In the accomplished rearrangement of isopropenyl phenyl ethers, the postulated mechanism, based upon the changes in the inner energy potentials of the compounds suggested, is further enhanced by the fact that these migrations involve the passing from an isolated system of double bonds to a conjugated system. Examination of the structures I and IV indicates that the unsaturation of the alkenyl group of the ethers is not in conjugation with the double bonds in the cyclic nucleus, forming an isolated system. On the other hand, the phenol structures III and VI have the double bonds arranged in the form of conjugated systems. Henrich[26] states that substances which possess conjugated double linkages "are more highly saturated" than substances which possess two separate pairs of double bonds. This would account for the greater stability of the conjugated system and elucidates once more the tendency of the isopropenyl phenyl ethers to pass to the corresponding phenols under the proper conditions.

Experimental Part

Preparation of Isopropenyl Phenyl and Cresyl Ethers.—The isopropenyl phenyl and cresyl ethers were obtained by the action of isopropenyl bromide upon potassium phenolate (cresolate). 2,2-Dibromopropane was first prepared by the method of Friedel,[27] which consists in treating acetone with phosphorus dibromotrichloride. The dibromopropane was converted to isopropenyl bromide by the method of Réboul[28] whereby hydrogen bromide is eliminated by the use of sodium ethylate. The potassium phenolate was then prepared by adding a mole of potassium hydroxide to a mole of the phenol with mild heating. When a homogeneous system was obtained a mole of the isopropenyl bromide was slowly added and the whole refluxed for two hours. Water was then added to dissolve the potassium bromide, and the ether separated as a colorless liquid. On distillation at ordinary pressure the pure product was obtained.

Rearrangement of Isopropenyl Phenyl and Cresyl Ethers.—The ethers prepared

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[26] Henrich, "Theories of Organic Chemistry," Johnson and Hahn, John Wiley and Sons, Inc., New York, 1922, p. 38.

[27] Friedel, *Ann. chim. phys.*, [4] **16**, 356 (1869).

[28] Réboul, *ibid.*, [5] 14, 475 (1878).

in the above manner were rearranged according to the method found most satisfactory in this Laboratory for phenyl ethers.[29,15b] The ether was refluxed for five hours with a 10% solution of sulfuric acid in glacial acetic acid, where the quantity of sulfuric acid was equimolar to the ether. The reaction mixture was allowed to stand overnight. After transferring to a separatory funnel, a volume of salt solution somewhat greater than that of the reaction mixture was added and the liquid layer which separated was drawn off. This consisted of unrearranged ether and the substituted ether; this latter was extracted with a 10% caustic potash solution and reprecipitated with concentrated hydrochloric acid. An ether extract was made; this was dried with calcium chloride and the substituted phenol was obtained pure by distillation.

Preparation of Isopropenylphenols and Cresols by the Condensation Method.—The method employed in these condensations is a modification of that reported in earlier articles.[30] To a solution of molar quantity of allyl alcohol and of the phenol, a fifth mole of sulfuric acid was added drop by drop. The mixture was cooled in an ice-bath and well shaken throughout the addition of the acid. The reaction flask was then stoppered with a stopper containing a calcium chloride drying tube and slowly allowed to come to room temperature. After standing for one week, the reaction mixture, a hard reddish mass, was pulverized and then washed with cold water to remove unreacted allyl alcohol, sulfonic acids and sulfuric acid. The washed product, an orange-red solid was a polymer of the isopropenylphenol On distillation at ordinary pressure (slight decomposition took place), depolymerization was effected and a monomer was obtained as a colorless liquid which darkened on standing.

Catalytic Reduction of Isopropenylphenols and Cresols to the Corresponding Isopropyl Compounds.—With the use of a catalytic reduction apparatus a calculated quantity of hydrogen was allowed to react with a weighed sample of the unsaturated alkyl phenol in an absolute alcohol solution. A platinic oxide catalyst was employed. After the required amount of hydrogen had reacted the solution was decanted from the catalyzer, and the alcohol allowed to evaporate spontaneously, while the solution was kept free from dust. The resulting product was then fractionally distilled to yield the pure isopropylphenol.[31]

Preparation of Phenoxy and Cresoxy Acetic Acids.—Two grams of the substituted phenol was added to one gram of solid potassium hydroxide dissolved in 15 cc. of water. This mixture was warmed on a water-bath until complete solution took place. Two grams of bromoacetic acid was dissolved in 10 cc. of water and 3 drops of phenolphthalein added; 10% potassium hydroxide was then added until a permanent pink color was obtained. The two solutions were then mixed and gently boiled for ten minutes. When cool, the mixture was placed in an ice-bath and neutralized with concentrated hydrochloric acid. Precipitation in the cold avoids the formation of undesirable oils. If an oil was formed, it solidified on standing. The product was then recrystallized from water.

Preparation of Bromine Derivatives.—These were prepared by treating the pure phenol with an excess of bromine in the cold, without the use of a solvent. The whole was then allowed to stand until all the hydrogen bromide and excess bromine had evaporated. The dark mass was then transferred to a porous tile and washed suc-

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[29] Niederl, Natelson and Smith, Indianapolis Meeting of the American Chemical Society, 1931; Niederl and Natelson, THIS JOURNAL, 54, 1068 (1932).

[30] Niederl, *ibid.*, 50, 2230 (1928); 51, 2426 (1929); *Z. angew. Chem.*, 44, 467 (1931); *Monatsh.*, 60, 150 (1932); Niederl and Casty, *ibid.*, 51, 1028 (1929); Niederl and Natelson, THIS JOURNAL, 53, 272 (1931); Smith and Niederl, *ibid.*, 53, 806 (1931); Niederl, Smith and McGreal, *ibid.*, 53, 3390 (1931).

[31] R. A. Smith, private communication, New York University.

TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

Compound	Formula	M. p., °C.	B. p., °C.	Sp. gr.	n_D	Analyses, % Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found
Products with Phenol									
Isopropenylphenyl ether[32]	$CH_2{=}C(CH_3)OC_6H_5$		169	0.998^{23}	1.5172^{23}	80.55	80.18	7.52	7.64
o-Isopropenylphenol (by rearrangement of above)[5]	$CH_2{=}C(CH_3)C_6H_4OH$		203–208	1.024^{28}	1.5452^{28}	80.55	80.23	7.52	7.25
o-Isopropenylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_4OH$		204–207	1.026^{28}	1.5448^{28}	80.55	80.18	7.52	8.36
Hexabromo-*o*-isopropenylphenol	$C_9H_4OBr_6$	84				17.73	17.40	0.82	0.97
o-Isopropylphenol (by reduction of *o*-isopropenylphenol)'	$CH(CH_3)_2C_6H_4OH$		212–214	1.016^{22}	1.5351^{22}				
o-Isopropylphenoxyacetic acid (from *o*-isopropylphenol)','	$CH(CH_3)_2C_6H_4OCH_2COOH$	130							
Products with *p*-Cresol									
Isopropenyl *p*-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		189–190	0.977^{27}	1.5118^{27}	81.03	81.38	8.17	8.39
2-Isopropenyl-4-methylphenol (by rearrangement of above)''	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		222–224	1.012^{24}	1.5362^{24}	81.03	80.73	8.17	8.00
2-Isopropenyl-4-methylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		223–226	1.009^{25}	1.5399^{25}	81.03	81.31	8.17	8.46
Products with m-Cresol									
Isopropenyl m-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		188–189	0.978^{21}	1.5117^{21}	81.03	80.66	8.17	7.91
5-Methyl-2 isopropenylphenol (by rearrangement of above)[6a,11]	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		225	1.026^{25}	1.5402^{25}	81.03	81.40	8.17	8.38
5-Methyl-2-isopropenylphenol (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		222–225	1.020^{26}	1.5360^{25}	81.03	81.21	8.17	8.53
$2,5,6,4^2,4^2$-Pentabromo-3-hydroxy-1-methyl-4-isopropenylbenzene'r	$CBr_2{=}C(CH_3)C_6Br_3(CH_3)OH$	103–104				22.32	22.09	1.62	1.29
x-Menthol (by reduction of 5-methyl-2-isopropenylphenol)	$C_{10}H_{20}O$		195–200			76.92	77.48	12.82	11.69
Products with o-Cresol									
Isopropenyl o-cresyl ether	$CH_2{=}C(CH_3)OC_6H_4CH_3$		184–185	0.983^{27}	1.5122^{27}	81.03	81.35	8.17	7.82
2-Methyl-4-isopropenylphenol (by rearrangement of above)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		225–228	1.026^{28}	1.5395^{28}	81.03	80.68	8.17	8.35
2-Methyl-4-isopropenylphenyl (by condensation)	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		224–228	1.029^{27}	1.5359^{27}	81.03	80.74	8.17	8.38
Pentabromo-2-methyl-4 isopropenylphenol	$C_{10}H_7OBr_5$	202				22.32	22.63	1.62	1.40
2-Methyl-4-isopropenylphenoxyacetic acid	$CH_2{=}C(CH_3)C_6H_3(CH_3)OCH_2COOH$	110–111				69.90	69.51	6.79	7.18
2-Methyl-4-isopropylphenol (by reduction of 2-methyl-4-isopropenylphenol)[6b,16]	$CH(CH_3)_2C_6H_3(CH_3)OH$		230–234	0.987^{20}	1.5138^{20}				
2-Methyl-4-isopropylphenoxyacetic acid	$CH(CH_3)_2C_6H_3(CH_3)OCH_2COOH$	140–141				69.23	68.95	7.69	7.98
Tetrabromo-2-methyl-4-isopropylphenol (from 2-methyl-4-isopropylphenol[a]	$C_{10}H_{10}OBr_4$	236–237				25.75	25.42	2.14	1.93

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[32] Ruhemann and Wragg, J. *Chem. Soc.*, **79**, 1190 (1901).

[a] The lustrous, golden-yellow plates obtained were shown to be identical with the 2,4,5-tribromo-6-hydroxy-1-methyl-3-isopropylbenzene, melting point 223°, reported previously by Niederl and Natelson. THIS JOURNAL, 53, **1931** (1931). It is postulated that it is also identical with the 2,4,5-tribromo-6-hydroxy-1-methyl-3-isopropylbenzene, melting point 221°, reported by Jesurun, *Ber.*, **19**, 1414 (1886), who offered no analysis for the compound.

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cessively with small quantities of benzene to remove the tarry material and last traces of bromine. Recrystallizations were then effected from alcohol or benzene.

The quantitative determinations were performed microanalytically according to Pregl.[33]

Summary

1. Short-chain alkenyl phenyl ethers (isopropenyl phenyl and cresyl ethers) were rearranged to the corresponding isomeric substituted phenols by means of a mixture of concentrated sulfuric and glacial acetic acids. Proofs for the structure of the products were advanced and a general rule as to the position of migration of the alkenyl side chain was postulated.

2. The rearranged products were resynthesized by the addition of the corresponding phenols to allyl alcohol. These extensions of this addition reaction show that addition of phenols to allyl alcohol is a general process.

3. A reaction mechanism was advanced for the rearrangement as well as for the addition reaction, involving the postulations of Van Alphen, Lapworth, Latimer and others.

4. The generally acknowledged rearrangement mechanism of Claisen for unsaturated alkyl phenyl ethers was found inapplicable to isopropenyl phenyl ethers. Preliminary work in the field of related compounds such as cinnamyl alcohol, cinnamyl chloride, the various cinnamyl phenyl ethers and esters, further indicate the insufficiency of the Claisen mechanism.

NEW YORK, N. Y.

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[33] Pregl, "Quantitative Organic Microanalysis," P. Blakiston's Sons and Co., Philadelphia, Pa.

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

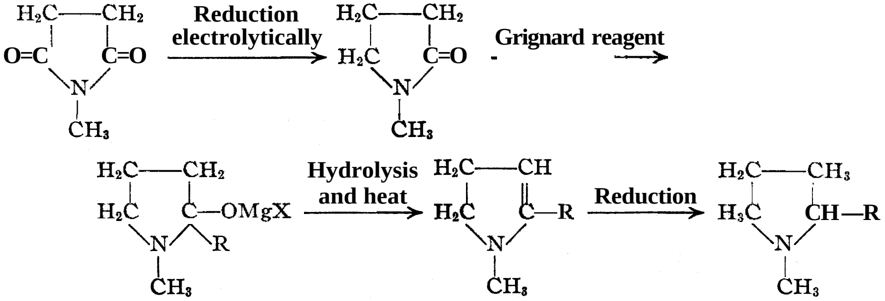
Synthesis of a Series of Alpha-Substituted N-Methylpyrrolines

BY LYMAN C. CRAIG[1]

Introduction

As part of a systematic study of structure and physiological action in the nitrogen heterocyclics it seemed desirable to prepare and study a series of a-substituted N-methylpyrrolidines. Although several members of the series have previously been prepared a suitable general method of synthesis was lacking.

Loffler[2] prepared several of the aliphatic members of the series by ring closure of a-substituted butylmethylamines but LaForge[3] was not able to effect ring closure of 1-methylamino-1-phenylbutane by the same method. Methylation of the corresponding a-substituted pyrrolidine offers another possibility since a general method of synthesis of a-substituted pyrrolidines has been given[4] but methylation of heterocyclic nitrogen is usually a poor and oftentimes impossible procedure from a synthetic standpoint. The following synthesis was proposed in this Laboratory and proved satisfactory for the preparation of the compounds in the quantity desired.



The α-substituted N-methylpyrrolines are intermediates in the above synthesis. As these compounds have been little studied[5] it seemed well to report their synthesis and properties in a separate preliminary paper.

a-Methylpyrroline has been found by Marz[6] to react with hydroxylamine, semicarbazide and phenylhydrazine in aqueous solution. The following equilibrium has been postulated to account for the reaction.

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(1) National Research Fellow.

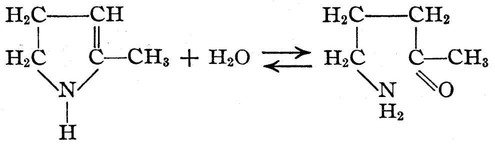
(2) Löffler, Ber., 43, 2046 (1910).

(3) LaForge, THIS JOURNAL, 60, 2471 (1928).

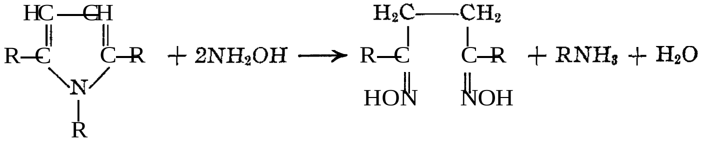
(4) Craig and Hixon, *ibid* , 53, 1831 (1931).

(5) While this work was under way the work of Lukes, *Collection Czechoslov. Chem. Comm.*, 2, 531-44, who synthesized several a-substituted N-methylpyrrolines by a similar method, appeared.

(6) Marz, Diss. Techn. Hochsch.. München, 1913.

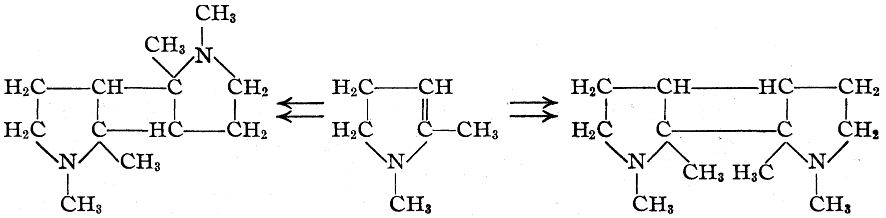


The same equilibrium has been found in the case of the analogous tetrahydropyridine series.[7] However, the compounds prepared in this Laboratory did not appear to exhibit the equilibrium. None of the series gave any indication of a reaction with semicarbazide or phenylhydrazine. When added to a solution containing equivalent quantities of hydroxylamine hydrochloride and potassium carbonate all of the derivatives readily dissolve but this fact cannot be taken as evidence for an equilibrium in the aqueous solution of the compound. A curious reaction of pyrrole derivatives with hydroxylamine according to the equation



has long been known.[8] It is only logical to expect that the half reduced pyrrole will act similarly with regard to the unreduced half of the ring. a-Methyl-N-methylpyrroline is the only member of the series that is soluble to any extent in water. All the other derivatives, when shaken with water and the layers separated, show little if any water to be present in the oily layer.

a-Methyl-N-methylpyrroline is the only member of the series which does not distil normally. Its behavior upon distillation can best be explained by a reversible polymerization to a dimer according to either or both of the following equations



This view is supported by the behavior of the compound upon reduction. The reduction products contain a 45% yield of a-methyl-N-methylpyrrolidine but also a 50% yield of a compound boiling at 132–134° (20 mm.). Analysis shows the compound to have the empirical formula $(C_8H_{12}N)_n$ which corresponds with that of the dipyrrolidine expected from either of

(7) Lipp and Widmann, *Ann.*, 409, 90 (1915).

(8) Ciamician and Zanetti, *Ber.*, 22, 1968 (1889); 23, 1787 (1890); Fischer and Zimmermann, *Z. physiol. Chem.*, 89, 163 (1924).

the two postulated dimers if the unstable cyclobutane ring is ruptured. It has been shown by Lipp[9] that the analogous compound N-methyltetrahydropicoline polymerizes to a dimer which dissociates again quite easily.

As a class the a-substituted N-methylpyrrolines are all unstable and quickly develop a deep red color after distillation when exposed to the atmosphere. However, they may be preserved colorless indefinitely if carefully sealed in ampoules with the exclusion of air. They are soluble in all organic solvents but insoluble in water with the exception of a-methyl-N-methylpyrroline, which is soluble in almost all proportions. They have a characteristic unpleasant odor.

Reduction of the series of a-substituted N-methylpyrrolines will be reported in a later paper.

The writer wishes to thank Professor E. Emmet Reid for his encouragement and advice during this work.

Experimental

Synthesis of N-Methyl-a-pyrrolidone.—This compound was first synthesized by Tafel and Wassmuth;[10] later by Spath and Bretschneider.[11] They reduced succinimide electrolytically at a lead cathode using a high current density. The resulting pyrrolidone was converted to the sodium derivative and methylated with methyl iodide or sulfate. A much more convenient synthesis is the electrolytic reduction6 of N-methylsuccinimide[12] by the method of Tafel and Stern.[13] The reduction product is isolated from the 50% sulfuric acid solution by a continuous extractor which is a modification of the Soxhlet extractor designed to extract aqueous solutions by chloroform. This method of isolation almost doubles the yield obtained by the method of Lukes.[5] Fractionation of the chloroform extract gives a yield of 80% of the theoretical amount of N-methyl-a-pyrrolidone boiling at 94–96" (20 mm.) and a small amount of unreduced succinimide.

Synthesis of a-Substituted N-Methylpyrrolines.—The Grignard reagent is prepared in the usual way using 2 moles of RX. One mole of pyrrolidone in an equal volume of ether is added dropwise. The mixture is allowed to stand overnight and hydrolyzed with an equivalent of hydrochloric acid. The aqueous layer is treated with excess sodium hydroxide solution and steam distilled. The base recovered from the distillate is dried over solid potassium hydroxide.

TABLE I

Compounds		Analysis, % Calculated C	H	Found C	H
α-Phenyl-N-methylpyrroline	$C_{11}H_{13}N$	82.4	8.24	82.7	8.5
α-*n*-Butyl-N-methylpyrroline	$C_9H_{17}N$	77.5	12.3	77.3	12.2
α-*n*-Propyl-N-methylpyrroline	$C_8H_{15}N$	76.7	12.0	76.4	12.0
α-Ethyl-N-methylpyrroline	$C_7H_{13}N$	75.7	11.8	75.5	12.5
α-Methyl-N-methylpyrroline	$C_6H_{11}N$	74.3	11.4	74.2	11.1

In the following table which describes some properties of the series the percentage yield is calculated on the weight of N-methyl-a-pyrrolidone used.

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(9) Lipp, *Ann.*, 289, 218 (1896).

(10) Tafel and Wassmuth, *Ber.*, 40, 2839 (1907).

(11) Spath and Rretschneider, *ibid.*, 61, 330 (1929).

(12) Menschutkin, *Ann.*, 182, 90 (1876).

(13) Tafel and Stern, *Ber.*, 33, 2224 (1900)

TABLE II

Compounds	Yield, %	B. p., °C.	Picrate	Oxalate
a-Phenyl-N-methylpyrroline	70	105–109 (11 mm.)	M. p., 139°	M. p., 138"
a-n-Butyl-N-methylpyrroline	54	86–87 (30 mm.)	M. p., 66°	Oil
a-n-Propyl-N-methylpyrroline	50	176–177	Oil	Oil
a-Ethyl-N-methylpyrroline	53	148–149	M. p., 114°	Oil
α-Methyl-N-methylpyrroline	50	130–131	Decd. upon heating	Oil

The measurement of other physical properties of the series is impracticable due to the speed with which the colorless freshly distilled base decomposes or reacts with the atmosphere. a-Methyl-N-methylpyrroline does not always distil in the same way in separate preparations. While in one run it distils completely at 130°, in another it cannot be distilled at atmospheric pressure. This run, at 30 mm. pressure does not give a well-defined distillation but the entire lot distils over, the temperature reaching as high as 140° (30 mm.) depending on the rate of distillation. The entire distillate comes over at 125–130° at atmospheric pressure when immediately redistilled.

Hielscher[14] first prepared a-methyl-N-methylpyrroline by ring closure of $CH_3COCH_2CH_2CH_2NHCH_3$. He reported that the compound could not be distilled under atmospheric pressure but gave no explanation of its instability. LaForge[3] reported the preparation of α-phenyl-N-methylpyrroline. The properties of a-n-propyl- and a-ethyl-N-methylpyrroline correspond substantially with those reported by Lukes.[5] α-*n*-Butyl-N-methylpyrroline could not be found in the literature.

Summary

N-methylsuccinimide was reduced electrolytically and N-methyl-α-pyrrolidone recovered in a yield of 80% of the theoretical.

A series of a-substituted N-methylpyrrolines have been prepared and their properties discussed. a-Substituted N-methylpyrrolines were not found to react with water in aqueous solution to give amino ketones and an explanation of the reaction with hydroxylamine in aqueous solution has been given.

α-Methyl-N-methylpyrroline has been shown to polymerize to a dimer which dissociates again quite easily.

BALTIMORE, MARYLAND

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[14] Hielscher, *Ber.*, 31, 277 (1898).

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Structure of Reactants and the Extent of Acetal Formation

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A study of the relationship between the concentration at equilibrium in the acetal reaction and the structure of the alcohol and aldehyde has been continued, particularly with reference to the effect of the structure of the alcohol upon the extent of its reaction with tetrahydrofurfural.[1,2] The object of the experimentation was to measure the effect of various typical structures upon carbon to oxygen linkages.

Tables I and II contain a summary of all the reliable data, obtained in this Laboratory during the past ten years, upon the effect of the structure of the alcohol and aldehyde upon the conversion at equilibrium in the acetal

TABLE I

REACTION OF ACETALDEHYDE AND TETRAHYDROFURFURAL WITH VARIOUS ALCOHOLS

			Acetaldehyde			Tetrahydrofurfural		
Alcohol	B. p., °C.	Mm.	Moles alc. per mole of ald.	% Conv.	K_e	Moles alc. per mole of ald.	% Conv.	K_e
Phenylpropyl	127–130	17	11	99 M	13.30	5	95 M	9.48
n-Octyl	189–190	740	..	...	...	5	95 M	9.48
n-Hexyl	154–157	738	..	...	...	5	95 M	9.48
n-Lauryl	M. p. 24		..	...	...	5	90 M	4.03
Isoamyl	4344	11	11	99 M	13.30	.	...	...
β-Aminoethyl			..	.. S	6.85	.	...	...
n-Amyl	134–135	740	11	98 M	6.48	5	89 M	3.55
β-Phenylethyl	120–121	27–30	11	98 M	6.48	5	89 M	3.55

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[1] Adkins and Wade Adams, THIS JOURNAL. 47, 1368 (1925); Hartung and Adkins. *ibid.*. 49, 2517 (1927); Street and Adkins, *ibid.*. 50, 162 (1928); Adkins and Broderick. *ibid.*, 50, 178 (1928); Adkins, Semb and Bolander, *ibid.*, 53, 1853 (1931).

[2] There has apparently been little done outside of this Laboratory upon the effect of the structure of the reactants upon the concentration at equilibrium in the acetal reaction. Attention should, however, be called to the very extensive studies of Skrabal and co-workers upon the rate of hydrolysis of acetals in rather dilute water solutions [Z. *Electrochem.*, 33, 322 (1928), and *Z. physik. Chem.*, 122, 357 (1926)]. The work of Herold and Wolf [*ibid.*, B5, 124 (1929), B12, 165 (1931)] upon the extent of hemiacetal formation as measured by absorption in the ultraviolet is also of interest. Their observations upon the effect of structure upon the extent of the hemiacetal reaction are, for the fifteen cases which they studied, in general agreement with the observations made in this Laboratory upon the extent of the acetal reaction with the same pairs of reactants. However, their prediction that the alcohols of higher molecular weight would show a decreasing affinity for acetal formation is not borne out by observations herewith reported. Further, their view that the efficacy of calcium chloride as a catalyst for the acetal reaction is due to its removing water from the sphere of reaction is not in accord with the results previously reported [Adams and Adkins, THIS JOURNAL, 47, 1358 (1925)] upon experiments intended to test out that hypothesis. They have apparently overlooked this paper as well as another upon hemiacetal formation [Adkins and Broderick. *ibid.*. 50, 499 (1928)].

TABLE I (Concluded)

			Acetaldehyde			Tetrahydrofurfural		
Alcohol	B. p., °C.	Min.	Moles alc. per mole of ald.	% Conv.	K_e	Moles alc. per mole of ald.	% Conv.	K_e
β-Phenylethyl			5	92 M	5.38	.	...	...
n-Heptyl	80–82	16–17	5	92 M	5.38	5	95 M	9.48
n-Heptyl			..	...	...	3	87 M	11.40
n-Butyl	114–115	740	11	96 B	3.08	5	80 M	1.44
n-Butyl			11	96 M	3.08	.	...	...
Tetrahydrofurfuryl	85–86.5	28	..	...	...	5	80 M	1.44
Isobutyl	106	738	11	96 M	3.08	5	78 M	1.22
Isobutyl			11	(93 A)	...	.	...	...
Methyl	63.5–64	739	11	95 B	2.41	5	86 M	2.34
Methyl			11	94 A	1.95	.	...	...
Ethyl	77–77.5	738	11	92 H	1.40	5	79 M	1.26
Ethyl			11	91 B	1.21	.	...	...
Ethyl			11	91 A	1.21	.	...	...
Ethyl			11	91 M	1.21	.	...	...
β-Iodoethyl			11	91 S	1.21	.	...	...
n-Propyl	95–96	740	11	90 A	1.06	5	80 M	1.44
n-Propyl			11	90 S	1.06	.	...	...
β-Chloroethyl	128	740	11	90 M	1.06	5	76 M	1.04
β-Chloroethyl			5	76 M	1.04	.	...	...
β-Chloroethyl			3	62 M	1.10	.	...	...
β-Ethoxyethyl			11	89 S	0.94	5	79 M	1.26
β-Methoxyethyl	121–122	740	11	89 S	.94	5	72 M	0.77
Benzyl	199–200	734	11	89 M	.94	5	79 M	1.26
Allyl	94–95.5	738	11	88 S	.84	5	72 M	0.77
β-Bromoethyl			11	87 S	.76	.	...	...
β-Nitroethyl			11	83 S	.52	.	...	...
Cyclohexylcarbinol	84	13	5	56 M	.26	.	...	...
Cyclohexanol	157–158	740	5	56 M	.26	5	88 M	3.15
Pentanol-2	116–117.5	738	11	72 M	.23	.	...	...
β-Carbethoxyethyl			11	66 S	.155	.	...	...
Butanol-2	98–99	738	11	64 H	.136	5	65 M	0.47
Butanol-2			11	63 M	.128	.	...	...
Octanol-2	78	12	5	46 M	.130	5	90 M	4.03
Octanol-2			..	...	...	3	86 M	4.30
Propanol-2	80–80.5		11	59 H	.101	5	49 M	0.166
Propanol-2			11	60 B	.107	.	...	...
Tert.-butyl	81.5	738	5	23 M	.019	5	38 M	0.073
Tert.-butyl			11	31 A	.015	.	...	...
Tert.-amyl	100	738	11	21 A	.006	.	...	...
Tert.-amyl			11	21 M	.006	.	...	...
β-Cyanoethyl	129–131	33	..	...	...	5	32 M	0.045

reaction. The data for the eighty-five acetals have been arranged in two tables, the first containing the data for the acetals of acetaldehyde and tetrahydrofurfural and the second for a miscellaneous group of acetals. The acetals are arranged in Table I in the order of decreasing value of K_e for acetals of acetaldehyde, and in Table II simply in order of decreasing

TABLE II

EXTENT OF REACTION OF VARIOUS ALCOHOLS AND ALDEHYDES

Alcohol	Aldehyde	Moles alc. / Moles ald	% Couv	K_e
Isobutyl	*n*-Butyr-	11	(96 A)	
Isobutyl	n-Butyr-	11	98 M	6.48
Methyl	n-Butyr-	11	(96 A)	
Methyl	n-Butyr-	11	97 M	4.22
n-Propyl	n-Butyr-	11	94 A	1.95
Ethyl	Aminoacet-	11	93 H	1.63
Ethyl	Hept-	10	92 H	1.37
Ethyl	Cyanacet-	13	93 H	1.30
Ethyl	Bromoacet-	11	91 H	1.21
n-Butyl	n-Butyr-	11	91 M	1.21
Ethyl	n-Butyr-	11	(92 A)	
Ethyl	n-Butyr-	11	91 H	1.21
Ethyl	n-Butyr-	11	91 M	1.21
Ethyl	Propion-	11	(89 A)	
Ethyl	Propion-	11	91 H	1.21
Ethyl	Isobutyr-	11	(84 A)	
Ethyl	Isobutyr-	11	86 M	0.68
Heptyl	Furfur-	5	68 M	.58
Ethyl	β-Chloroprop-	11	84 H	.56
Ethyl	Glycolic	11	75 H	.28
Butanol-2	n-Butyr-	11	74 M	.26
Octanol-2	n-Butyr-	5	53 M	.20
Ethyl	Acrylic	11	68 H	.176
Octanol-2	Benz-	5	49 M	.160
Methyl	Furfur-	11	61 A	.114
Methyl	Furfur-	5	42 Bl	.100
Cyclohexylcarbinol	Isobutyr-	5	42 M	.100
n-Butyl	Benz-	11	56 Sb	.083
Ethyl	Benz-	11	56 Sb	.083
Propanol-2	n-Butyr-	11	(59 A),	
Propanol-2	n-Butyr-	11	53 M	.069
Propanol-2	Propion-	11	50 A	.057
Ethyl	Furfur-	11	44 Bl	.039
Ethyl	Furfur-	11	45 M	.041
Ethyl	m-Nitrobenz-	11	42 A	.034
Tert.-butyl	n-Butyr-	11	38 M	.026
Propanol-2	Isobutyr-	11	(37 A)	
Propanol-2	Isobutyr-	11	33 M	.018
Ethyl	Cinnam-	11	(36 A)	
Ethyl	Cinnam-	11	29 H	.013
Ethyl	Croton-	11	27 H	.011
Propanol-2	Furfur-	11	25 A	.009
Propanol-2	Benz-	11	19 Sb	.005
Propanol-2	Cinnam-	11	19 A	.005
Tert.-butyl	Isobutyr-	11	18 M	.004
Octanol-2	Furfural	5	11 M	.003
Tert.-butyl	Furfural	6	OM	.000

value of K_e. The observer of each reaction mixture has been indicated by a letter placed after the percentage conversion for the acetal (**A** for Adams B for Broderick, Bl for Bolander, H for Hartung, M for Minné, S for Street and Sb for Semb).[3]

One of the primary objects of this investigation was to ascertain whether, if an alcohol, for example, gave the same percentage conversion at equilibrium with two aldehydes, a second alcohol would give the same conversion with one aldehyde as with the other. In seeking an answer to this question nineteen alcohols have been tested with acetaldehyde and tetrahydrofurfural. Among these there is fair agreement in fifteen cases between the values of K_e for the reaction of the alcohol with the two aldehydes. With eight of these fifteen alcohols there is almost perfect agreement, that is to say, the percentage conversion at a given ratio of reactants is not more than 1% different for one aldehyde than for the other. However, the four secondary and tertiary alcohols listed below show a very different conversion with acetaldehyde as compared with tetrahydrofurfural: cyclohexanol, 56 and 88%; butanol-2, 46 and 65%; octanol-2, 46 and 90%; *tert.*-butyl, 23 and 38%. These results indicate very definitely that the relative affinity manifested by two compounds for the formation of a given type of linkage is not independent of the second component of the reaction.

The effect of lengthening the chain of the alcohol is not so clear in the case of the data for acetaldehyde as it is for tetrahydrofurfural, since most of the determinations for the former aldehyde were made for such a high ratio of alcohol to aldehyde that the conversions for this type of alcohol are so high that small differences between alcohols are not apparent. The values of K_e for tetrahydrofurfural and the primary alcohols with normal chains and the carbon content indicated in parentheses are: (1) 2.34, (2) 1.26, (3) 1.44, (4) 1.44, (5) 3.55, (7) 9.48, (8) 9.48, (12) 4.03. The values for the same aldehyde with three secondary alcohols are propanol-2, 0.166; butanol-2, 0.47; and octanol-2, 4.03. Somewhat similar values hold for the reaction of four secondary alcohols with acetaldehyde. These values

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[3] All of the values for K_e reported by Adams, Broderick, Hartung and Street have been recalculated and a majority of them have been checked by experiment if two observers had not previously done so. The values of K_e were recalculated upon the basis of concentrations expressed in mole fractions. The values of K_e reported in the earlier papers were calculated upon concentrations of moles per liter and comparisons between aldehydes made upon the calculated values of the decrease in free energy. These original calculations were ill advised for two reasons. First, compounds which show the same percentage conversion but have a different molecular volume will have therefore different values of K_e, and so appear to have different affinity values when as a matter of fact they are identical in their chemical behavior in the acetal reaction. Second, the use of values for the decrease of free energy so calculated adds nothing significant to the comparison of aldehydes and alcohols in the acetal reaction and is open to misinterpretation.

indicate that affinity in acetal formation first decreases slightly with increase in length of the carbon chain and then materially increases.

Simple branching of the chain has relatively little effect upon the extent of the acetal reaction. Isobutyl alcohol with acetaldehyde and *n*-butyraldehyde shows values which are not essentially different from those for butanol-1. Isobutyraldehyde has a lower value than n-butyraldehyde but very little lower than propionaldehyde, which has the same length of chain. However, branching of the carbon chain as exemplified in the cyclohexyl group is rather effective in lowering affinity for acetal formation. Five moles of cyclohexylcarbinol reacted with one mole of acetaldehyde to the extent of only 56% while hexylcarbinol, having the same carbon content, reacted to the extent of 92%. A similar negative though less marked effect of the cyclohexyl group was observed in the reaction of cyclohexylcarbinol with isobutyraldehyde. It was surprising that cyclohexylcarbinol reacted to a less extent with acetaldehyde than did phenylcarbinol despite the unsaturation and general negative character of the benzenoid nucleus.

The effect of an alkene linkage in a molecule either of an alcohol or an aldehyde, but especially the latter, was very marked in lowering affinity for the acetal reaction. Tetrahydrofurfural with ethanol had a value of K_e of 1.26, while furfural had less than one-half the percentage conversion with a value for K_e of 0.041. Propionaldehyde and butyraldehyde had 1.21 while the corresponding unsaturated aldehydes had 0.176 (acrolein) and 0.011 (crotonaldehyde). Benzaldehyde was almost identical with acrolein, and cinnamic aldehyde with crotonaldehyde. Unsaturation in the alcohol was apparently much less effective, as allyl alcohol was 0.54 with acetaldehyde, and 0.77 with tetrahydrofurfural, values which are not so much lower than for propanol-1, *i.* e., 1.06 and 1.44.[4]

The primary alcohols, if there were no complicating substituent, reacted with acetaldehyde to the extent of about 90% at a ratio of one mole of aldehyde to 5 moles of alcohol, while secondary alcohols gave conversions less than one-half as great. Simple tert. alcohols reacted with acetaldehyde to about one quarter the extent of the primary alcohols, the value of K_e for n-butyl, *sec.*-butyl and *tert.*-butyl being 3.08, 0.136 and 0.019, respectively. However, with alcohols and aldehydes of more complicated structure these relationships are far from being so simple. For example, cyclohexylcarbinol, a primary alcohol, behaved like a *sec.* alcohol in its reaction with acetaldehyde and isobutyraldehyde, having values of K_e of 0.26 and 0.100. Similarly octanol-2 behaved like a simple secondary alcohol with acetaldehyde (K_e 0.130) but with tetrahydrofurfural it had a value of 4.03, which is materially higher than that shown by the simple

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[4] It must be kept in mind that while unsaturation *decreased* the extent of the acetal reaction it greatly *enhanced* the rate of the reaction. Furfural, for example, reacted several hundred times as rapidly as tetrahydrofurfural under the same conditions but it proceeded less than one-half as far.

primary alcohols. Octanol-2 also gave a higher conversion with benzaldehyde than did any of the primary alcohols. In contrast with the abnormally high value of octanol-2 for benzaldehyde and tetrahydrofurfural was its abnormally low value (0.003) for furfural, with which it reacted to less than half the extent of propanol-2.

The effect of the phenyl group upon the acetal reaction might be ascribed to a combination of unsaturation and branching of the carbon chain but it seems simpler to regard it as a substituent. If the phenyl group in benzyl alcohol is regarded as substituted in methanol, then it had a small influence in decreasing the reaction with acetaldehyde or tetrahydrofurfural to the extent of about 7%. However, when substituted in ethyl or propyl alcohol the phenyl group increased the extent of the acetal reaction just as did the corresponding large alkyl groups. When directly attached to the aldehyde group as in benzaldehyde, the affinity of the aldehyde for acetal formation was low, being only 56% with 11 moles of ethanol to 1 mole of benzaldehyde, and not much greater than that given by furfural. When the phenyl group was further from the aldehyde group, as in cinnamic aldehyde, it was almost without effect since crotonic and cinnamic aldehydes gave approximately the same conversions with ethanol.

Certain substituents in ethanol show the following values of K_e in the reaction with acetaldehyde: iodo the same as the unsubstituted ethanol, 1.21, chloro 1.06, methoxy and ethoxy 0.94, bromo 0.76, nitro 0.52, and carbethoxy 0.155. When some of these groups were substituted in acetaldehyde they showed the following values for K_e in the reaction with ethanol: amino 1.63, cyano 1.30, bromo 1.21 and chloromethyl 0.56. The most striking effect was the negativity of the cyano group in β-cyanoethyl alcohol (ethylene cyanohydrin), which reacted with tetrahydrofurfural to the extent of only 32% ($K_e = 0.045$).

The extents of the reactions of the three methylcyclohexanols with tetrahydrofurfural were also determined. Samples of the three structural isomers (each a mixture of geometrical isomers) were obtained from the Eastman Kodak Company and upon fractionation showed the following boiling points: 2-methylcyclohexanol 162–163.5°, 3-methylcyclohexanol 168.5–170°, 4-methylcyclohexanol 169.5–171.5°. These compounds just after distillation gave the following conversions to acetal when allowed to react (5 moles) with tetrahydrofurfural (1 mole): 2-methylcyclohexanol 85%, 3-methylcyclohexanol 50% and 4-methylcyclohexanol 60%. Samples of the 2-methyl and the 4-methyl compound prepared in this Laboratory by hydrogenation of the corresponding phenols over nickel at 175°, 120–200 atmospheres, and having the same boiling points as the Eastman products, gave conversions in the acetal reaction of 87 and 82%, respectively. The first of these values is in good agreement with that obtained with the Eastman product while the value for the 4-methyl compound is

22% higher than previously observed. Moreover, the sample of the 3-methyl compound gave, when allowed to stand for several months after distillation and before use, a conversion of 68%, or 18% higher than when freshly distilled. All of these variations are understandable since it is well known that different methods of hydrogenation produce different proportions of isomers, and that one geometrical isomer is labile, so that changes in their proportion may occur on standing. The conclusion seems inescapable that different geometrical isomers show different affinity values for acetal formation although this must be confirmed by ascertaining the affinity for acetal formation of the pure cis and *trans* isomers of the three structurally different methylcyclohexanols.[5]

Experimental Part

Tetrahydrofurfural has apparently not hitherto been prepared in any considerable quantities. Scheibler, Sotscheck and Friese[6] prepared as much as 6 g. of "crude product" in a single experiment and unreported amounts of a relatively pure compound. The quantities needed for the investigation described herewith were relatively large so that it was necessary to make a thorough study of its preparation. Bolander[1] worked out the first step, *i.* e., the preparation of furfural acetal. The procedure for the hydrogenation of furfural acetal in good yield to tetrahydrofurfural acetal over a nickel catalyst was developed by Covert and Connor.[7] The third step in the preparation of the desired aldehyde, that is, the hydrolysis of tetrahydrofurfural acetal, proved to be a difficult one because of the readiness with which the aldehyde is resinified and also because of the difficulty of separating it from the alcohol and water in the mixture after hydrolysis. It appears unnecessary to give a detailed account of the various modifications of the procedure which were made in developing a satisfactory process, so it must suffice to describe briefly the preferred procedures.

One mole (174 g.) of diethyl tetrahydrofurfural acetal with 15 moles of water (270 g.) and 0.015 g. of hydrogen chloride were placed in a 2-liter 3-necked flask provided with a reflux condenser, a mechanical stirrer with a mercury seal, and a thermometer. The reaction mixture was heated on a steam-bath at 80° with stirring for five to ten hours, the mixture being homogeneous after about one hour. When hydrolysis was complete, as determined by a titration of an aliquot by the sodium sulfite method, the hot solution was left just acid to litmus by almost neutralizing with solid sodium carbonate (about 0.5 g.). It was found advisable to calculate the amount of sodium carbonate necessary by titrating an aliquot with 0.02 N sodium carbonate solution using methyl orange as an indicator. The reaction mixture was then rapidly cooled and 150 g. of anhydrous sodium sulfate added. After several hours the liquid was filtered off the sodium sulfate and another portion of the drying agent added. The process was repeated until 500 g. of sodium sulfate had been used, the drying process requiring twenty-four hours. The dried product was then fractionated at 6–10 mm. from a 250-ml. flask through a Widmer column having a spiral 24 cm. in length. The fraction 25–35" was about 60% aldehyde, while that from 35–45" was fairly pure. The lower fraction was dried with sodium sulfate together with the aldehyde (5–10 g.) extracted with ether from the 500 g. of sodium sulfate used earlier in the process. All the aldehyde was then carefully refrac-

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[5] The separation of the isomers has just been reported. Skita and Faust, *Ber.*, 64B, 2878 (1931); Hückel and Hagenguth, *ibid.*, 2892.

[6] Scheibler, Sotscheck and Friese, *ibid.*, 57, 1443 (1924); *ibid.*, 58, 1961 (1925).

[7] Covert, Connor and Adkins, THIS JOURNAL, 54, 1655 (1932).

tionated, from 35 to 50 g. being obtained, b. p. 35–37° (8 mm.). The excess water may also be largely removed by fractionation at 25–32° (13–15 mm.) through a Widmer column having a spiral 35 cm. in length and the residue dried as described above. About 15–20% of the aldehyde was lost in the water distillate but the yield of aldehyde obtained was about the same as by the less tedious process described above.

The yield of diethyl furfural acetal from furfural was from 15 to 20%, the yield of the tetrahydrofurfural acetal was 75 to 80%, while the conversion of the latter to tetrahydrofurfural in eight preparations was 35 to 50%. This is an over-all yield of 4 to 8% of tetrahydrofurfural based upon the furfural.

Tetrahydrofurfural is a colorless, somewhat viscous liquid of acrid though not sharp odor. It has the following constants: b. p 144–145° corr. (740 mm.); d_4^{25} 1.10947, n_D 1.4700 to 1.4708; M_D 24.54, calcd., 24.72. Samples of the aldehyde during the course of several weeks became yellow, solid particles appeared and formic acid was apparently produced. The aldehyde showed no signs of change at 20–25° in a desiccator during the course of a week. Scheibler, Sotscheck and Friese in their first publication on tetrahydrofurfural gave the following constants: b. p. 45–47" (29 mm.), b. p. 142–143' (779 mm.), d_4^{20} 1.0501, *n*, 1.47036, M_D 26.60. In their second paper they report d_4^{20} 1.0727, n_D 1.43658, M_D 24.43. The writers found that products of n_D 1.4330 to 1.4350 showed a lower tetrahydrofurfural content by titration than did the product n_D 1.4700–1.4708.

Di-(β-Ethoxyethyl) Acetal of **Tetrahydrofurfural.**—The di-(β-ethoxyethyl) acetal of furfural was prepared from furfural and β-ethoxyethanol (cellosolve) by the method described for the diethyl acetal. Three moles of furfural, 18 moles of cellosolve and 0.0036 g. of hydrogen chloride were allowed to react for four days until the conversion to the acetal was 40% of the theoretical. The water, cellosolve and furfural were then largely removed by distillation up to 76° at 18 mm. through a Widmer column. The residue was then fractionated at 2 to 4 mm. through a heated Widmer column. A yield of 212 g. of acetal (27.4%), b. p. 131–132° (2 mm.), 259" (740 mm.) was obtained.

The acetal (104 g.) was hydrogenated during the course of four hours at 150°, 130–200 atm., over 4 g. of a nickel catalyst of the ammonium carbonate type.[4] The product was fractionated twice through an electrically heated Widmer column. Twenty-eight grams (69%) of di-(β-ethoxy ethyl) acetal of tetrahydrofurfural, b. p. 131–136" (4–5 mm.), was obtained. There was an additional yield of slightly impure material corresponding to 8%. The compound was analyzed not only for carbon and hydrogen (see Table III) but a weighed sample was also subjected to hydrolysis and the tetrahydrofurfural so produced titrated. The amount of aldehyde formed was 98.8% of the amount calculated from the weight of acetal taken. Cellosolve (4.5%) (0.044 mole) and the β-ethoxyethyl ether of tetrahydrofurfuryl alcohol (6.7%) (0.040 mole) were also produced during the process of hydrogenating the acetal of furfural. The correspondence in molecular equivalents of cellosolve and ether formed indicates that these two compounds may be considered to be formed as in the hydrogenation and splitting of ethyl furfural acetal.[4]

Determination of the Concentration of Aldehydes.—The sodium sulfite method of titration was used for the determination of all the aldehydes except benzaldehyde, for which the hydrogen peroxide method was used. The acid solution for the sulfite method was not only standardized against the appropriate aldehyde but in the presence of the alcohol which would be in the sample later submitted to analysis. The ratio of alcohol to aldehyde in the sample used for standardization should be the same as that in the sample to be analyzed. The importance of this is evidenced by the following. A solution of sulfuric acid which was 0.202 *N* against sodium carbonate was 0.241 N against furfural, 0.2335 N against tetrahydrofurfural and 0.222 N against acetaldehyde, in the presence of ethanol. However, in the presence of an alcohol (in the ratio of alcohol to aldehyde which existed at equilibrium starting with the reactants in a 5 to 1 ratio) the normality figure for tetrahydrofurfural must be multiplied by 1.008 for cellosolve, 1.22 for heptyl, 1.72 for benzyl, 1.85 for phenylethyl and 3.64 for phenylpropyl alcohol. The factor for furfural in the presence of heptyl alcohol was 1.19 and 1.18 for octanol-2.

The procedure used in carrying out the studies on concentration at equilibrium was essentially the same as that previously described except in a few particulars. In the case of acetaldehyde a known weight of the aldehyde was sealed up in a glass tube and cooled to 0° before it was introduced into the alcohol. In the case of acetaldehyde, n-butyraldehyde and isobutyraldehyde, a titration was made to ascertain the exact concentration of the aldehyde in the alcohol solution before the catalyst was added. The concentration of the catalyst, hydrogen chloride, was 5 milligrams per mole of aldehyde except that in order to secure a sufficiently rapid rate of reaction 100 milligrams of hydrogen chloride per mole of tetrahydrofurfural was used

Homogeneity of the Reaction Mixtures.—All of the reaction mixtures contained a considerable excess of alcohol over that required for the formation of an acetal. This was in order to prevent the separation of water formed in the reaction. However, the solubility of water in some of the alcohols of higher molecular weight is sufficiently low that it was feared that the high conversions to acetal observed were due in part to the separation of water. However, observations of the reaction mixture under a microscope at a magnification of 350 diameters, even after long standing, failed to show any lack of homogeneity. The solubility of water was found to be greater than 1 ml. in 25 ml. of heptanol-1, or 37.5 ml. of octanol-2. The amount of water formed by the reaction of either of these alcohols with tetrahydrofurfural never exceeded 1 ml. of water in 45 ml. of alcohol, so there seems no reason to doubt that the reaction mixtures were in all cases homogeneous.

Hydrolysis of Acetals.—There has never been any evidence for false equilibria or side reactions under the conditions of these studies. However, the extent of hydrolysis of the diethyl acetals of furfural and of tetrahydrofurfural and of the di-(β-ethoxyethyl) acetal of tetrahydrofurfural was determined. For example, 0.091 mole of diethyl furfural acetal. 0.091 mole of water, 0.27 mole of ethanol and 0.000465 g. of hydrogen chloride were allowed to react at 25°. Thirty-five per cent. of the acetal was hydrolyzed after twenty-five minutes, 55% after fifty minutes and 66% at the end of one and one-half hours; reaction ceased with a total hydrolysis of 67% of the acetal. This value is in excellent agreement with that for synthesis under similar conditions, although less than thirty minutes was required for the completion of synthesis

Similar experiments were conducted with the acetal of ethanol and of cellosolve with tetrahydrofurfural. The ratio of reactants was 0.01 mole of acetal, 0.03 mole of alcohol, 0.01 of water and 0.001 g. of hydrogen chloride. Hydrolysis had proceeded to equilibrium after about one month. In the case of cellosolve the hydrolysis was 20 to 22%. while for ethanol it was 20 to 21%. These experiments demonstrate again the enormous difference in the rate of reaction of furfural as contrasted with the saturated aldehydes, and also the greater speed of synthesis as compared with hydrolysis.

Isolation of Various Acetals.—Small amounts of a number of acetals of tetrahydrofurfural were isolated, from the reaction mixtures set up for the purpose of determining the extent of the reaction, in essentially the same manner as the ethyl acetal. These products were fractionated as carefully as the small quantity of material involved would permit but in a few cases they were perhaps not entirely free of the alcohol involved. Qualitative tests showed them in every case to be free of tetrahydrofurfural. Their boiling points were in general determined by the capillary tube method described by Kamm[8] except that the determination was made under reduced pressure. The sam-

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[8] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, p. 118.

ple was placed in a test-tube 1 cm. in diameter, which was attached to a small reflux condenser the outlet from which led to a vacuum pump. The data on the analysis and certain of the physical constants of these and other compounds not hitherto described are given in Table III.

Time for Attainment of Equilibrium.—The alcohols and aldehydes were allowed to react in a thermostat at 25°. The reaction of furfural and some of the other unsaturated aldehydes was complete after an hour or two, the saturated aldehydes other than tetrahydrofurfural after two days, while the latter required six to eight days. Titrations were usually begun after two days and continued at intervals of two days until variations in analyses were less than 0.5%. In many cases titrations made after several months confirmed the fact that equilibrium was attained in almost all cases after ten days. It was interesting to observe that tetrahydrofurfural, which in the pure state began to deteriorate after a week or so, appeared to remain unchanged for many months in the presence of alcohol.

Purification **of** Reagents.—The alcohols and aldehydes, other than those that have been described in the preceding paragraphs, were purified as previously described in this series of papers or by standard methods.

Reliability of Data in Tables I and II.—An experienced operator can readily duplicate analyses for aldehyde to within 0.5%, and duplicate his observations on the percentage conversion of an aldehyde to its acetal in different reaction mixtures to within less than 1%. In many cases, as indicated in the tables, different operators have observed percentage conversions which agreed to within less than 1%. However, it seems safer to attach no significance to variations in extents of conversion of less than 3%. The value of K_e changes very rapidly with small changes in the percentage conversion, so that if the latter is very high (93–95%), little significance should be attached to *variations* of K_e. The data on representative acetals presented by Semb and Bolander and in this paper show that the value of K_e is independent of the ratio of reactants and thus is a

TABLE III

ANALYSES AND PHYSICAL CONSTANTS

Compound	B. p., °C.	Mm.	n_D	d^{25}_4	M_D Calcd.	M_D Found	Calcd. % C	Calcd. % H	Found % C	Found % H
Acetals of acetaldehyde										
n-Heptyl($C_{16}H_{34}O_2$)	153	12	1.4288	0.8372	79.12	79.52	74.34	13.27	74.30	13.32
Phenylpropyl($C_{20}H_{26}O_2$)	182-185	2	1.5229	1.0049	90.95	90.64	80.50	8.72	80.32	8.94
Acetal of furfural										
β-Ethoxyethyl($C_{13}H_{22}O_5$)	131–132	2	1.4534	1 0374	67.48	67.27	60.42	8.59	60.03	8.59
Acetals of tetrahydrofurfural										
n-Amyl($C_{15}H_{30}O_3$)	145	9.5					69.70	11.71	69.71	11.67
n-Butyl($C_{13}H_{26}O_3$)	114	9.5					67.76	11.39	67.83	11.45
β-Ethoxyethyl($C_{13}H_{26}O_5$)	135	4	1.4403	1.0005	68 25	68 47	59.58	9.99	59.53	10.06
n-Hexyl($C_{17}H_{34}O_3$)	167-173	15	1.4433				71.26	11.97	71.08	11.95
Phenylethyl($C_{21}H_{26}O_0$)	195-198	3	1.5342				77.25	8.03	77.05	7.90
Phenylpropyl($C_{23}H_{30}O_3$)	226	9.6					77.94	8.54	78.02	8.67
Tetrahydrofurfuryl ($C_{15}H_{26}O_5$)	163	9.5					62.89	9.16	62.13	9.19
Ether										
α-(β-Ethoxy ethyl) Tetrahydrofurfuryl ($C_9H_{18}O_3$)	76	9	1.4360	0.9802	46.47	46.41	62.01	10.42	61.94	10.26

true equilibrium *constant. The redetermination and recalculation of results previously reported have led to the elimination as unreliable of the values previously given for isoamyl, β-phenylethyl and benzyl acetals of acetaldehyde, and for the n-butyl acetal of butyraldehyde. The percentage conversions reported for the first time in this paper represent on the average six analyses of three different reaction mixtures at equilibrium.

Summary

The extent of reaction of tetrahydrofurfural with a variety of alcohols has been determined and the extent of the reaction of a number of other aldehydes and alcohols has been determined or redetermined and all previous results on the extent of this reaction have been recalculated to a comparable basis. All of these results on the relation of structure to affinity in the acetal reaction have been summarized as briefly as is feasible in Tables I and II and in the ensuing discussion.

The relative reactivity of the secondary and tertiary alcohols with acetaldehyde and tetrahydrofurfural, and the behavior of cyclohexylcarbinol and the three methylcyclohexanols with acetaldehyde all point to an important conclusion, *i. e., the spacial characteristics of a molecule may be an important factor in determining the binding power at a linkage, just as it has long been known that space relationships may modify the rate at which a reaction proceeds. In other words, steric as well as structural factors determine the strength of bonds.*

A process has been developed for preparing tetrahydrofurfural of excellent quality in fair yields. A number of acetals not hitherto described are reported.

MADISON, WISCONSIN

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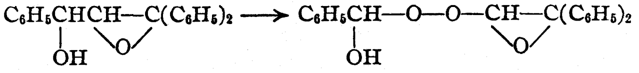
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Autoxidation of Certain Ethylene Oxides

BY E. P. KOHLER AND E. M. NYGAARD

In a recent paper we reported that when α,α-diphenyl-β-(hydroxybenzyl) ethylene oxide is exposed to the air it is oxidized to a peroxide.[1]

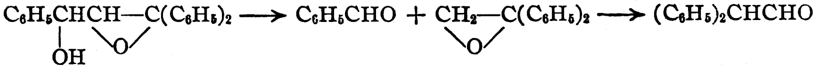


$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C_6H_5CH}}\underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH{-}C}}\mathrm{(C_6H_5)_2} \longrightarrow \underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C_6H_5CH}}\mathrm{{-}O{-}O{-}}\underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH{-}C}}\mathrm{(C_6H_5)_2}$$

This peculiar case of autoxidation first aroused our interest because it was erratic, some specimens apparently being perfectly stable in the air while others, which had been prepared in the same manner, were oxidized with sufficient rapidity to cause a perceptible rise in temperature. Another incentive to further investigation appeared when the structure of the oxidation product was definitely established, showing that the substance is a peroxide of the type that is usually obtained from free radicals.

We have found that the erratic character of the oxidation is not due to differences in the purity of the oxide but to variations in the quality of the air. No oxidation occurs either in air containing a trace of ammonia or in air that has been washed with bases, but when a little hydrogen chloride is added to the washed air, oxidation starts after a time and the principal product is the peroxide. The odor of benzaldehyde is perceptible whenever oxidation occurs, and benzoic acid, benzophenone and formic acid are always formed along with the peroxide.

We have found also that, in all probability, the function of the acid is to cleave the oxide—a rather surprising role in a reaction between a gas and a solid. In solutions containing a trace of base the oxide can be preserved indefinitely but in solutions containing even traces of acid it is rapidly destroyed in accordance with the equation



$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C_6H_5CH}}\underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH{-}C}}\mathrm{(C_6H_5)_2} \longrightarrow \mathrm{C_6H_5CHO} + \underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH_2{-}C}}\mathrm{(C_6H_5)_2} \longrightarrow \mathrm{(C_6H_5)_2CHCHO}$$

This transformation is complete and the process cannot be reversed either in the presence or the absence of a solvent. In solutions containing equivalent quantities of benzaldehyde and diphenylethylene oxide and a trace of base, both the aldehyde and the oxide slowly disappeared but no oxido alcohol was formed. When a solution of diphenylethylene oxide in an equivalent quantity of benzaldehyde was left to itself in an atmosphere of nitrogen, no change whatsoever occurred in the course of a month. When the solution was heated on a steam-bath the oxide slowly changed to diphenyl acetaldehyde but there was no condensation of the oxide and the aldehyde; and the addition of a few bubbles of hydrogen chloride merely accelerated the rearrangement of the oxide. But when a similar solution of

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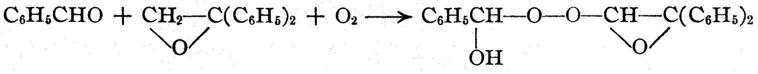
[1] Kohler, Richtmyer and Hester, THIS JOURNAL, 53,205 (1931).

the oxide in the aldehyde was exposed to the air it soon began to deposit a solid and it ultimately solidified completely. Under favorable conditions the solid contained nearly 50% of the possible amount of the peroxide, mixed with smaller quantities of the mono benzoate of diphenyl glycol, benzoic acid, benzophenone and formic acid. Here the peroxide is manifestly formed from the primary cleavage products of the oxide in accordance with the equation

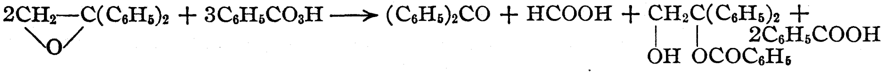


$$C_6H_5CHO + \underset{\diagdown O \diagup}{CH_2—C}(C_6H_5)_2 + O_2 \longrightarrow C_6H_5\underset{\underset{OH}{|}}{CH}—O—O—\underset{\diagdown O \diagup}{CH—C}(C_6H_5)_2$$

In this manner it was established that the oxide is not attacked by oxygen in the absence of acid, that acids cleave the oxide to benzaldehyde and diphenylethylene oxide, that the oxido alcohol cannot be regenerated from these cleavage products, and that in the air these primary cleavage products are oxidized to the peroxide The conclusion seems inevitable that the peroxide is formed in a series of reactions involving, first, cleavage of the oxide by acid, then autoxidation of the primary cleavage products, and finally synthesis of the peroxide from the products of oxidation.

The nature of the oxidation products from which the peroxide is formed is still somewhat mysterious. Diphenylethylene oxide is not attacked by free oxygen either in the presence or in the absence of acids. Benzaldehyde readily undergoes autoxidation being converted, first, into benzoperacid and finally into benzoic acid under all conditions hitherto investigated. Both of these oxidation products react with diphenylethylene oxide at the ordinary temperature but the reactions do not lead to the peroxide.

The reaction between benzoperacid and diphenylethylene oxide has been investigated with care by Meerwein and Bodendorf.[2] It is represented by the equation



$$2\underset{\diagdown O \diagup}{CH_2—C}(C_6H_5)_2 + 3C_6H_5CO_3H \longrightarrow (C_6H_5)_2CO + HCOOH + \underset{\underset{OH}{|}}{CH_2}\underset{\underset{OCOC_6H_5}{|}}{C}(C_6H_5)_2 + 2C_6H_5COOH$$

As will be seen, this reaction accounts for approximately half of the material and nearly all of the products that are formed in the autoxidation of the mixture of benzaldehyde and diphenylethylene oxide, but it does not account for the peroxide.

The experimental conditions under which the reaction was studied were quite different from those under which the peroxide is formed but differences in the experimental conditions could hardly account for oxidation to open chained compounds in the one case and the formation of the peroxide, in which the oxide ring is intact, in the other. Evidently benzoperacid—like benzoic acid—readily opens the oxide ring; after that has happened, the formation of the peroxide is impossible. For these reasons it seemed to us highly improbable that benzoperacid was an intermediate in the forma-

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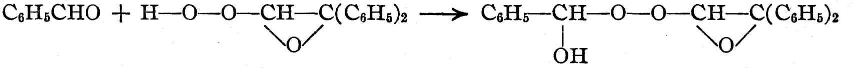
[2] **Bodendorf,** Dissertation, Königsberg, 1928.

tion of the peroxide, but we nevertheless decided to repeat the work of Bodendorf under conditions as nearly as possible like those which prevailed in the autoxidation of the cleavage products. To this end we prepared nearly pure benzoperacid by the method of Smit[3] and added it very slowly, in an atmosphere of nitrogen, to a solution of the oxide in benzaldehyde. The products were the same as those obtained by Bodendorf; no peroxide could be detected at any stage of the operation.

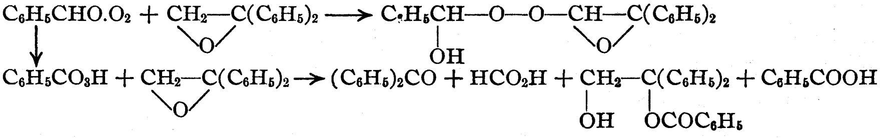
From the foregoing facts it is certain that benzoperacid is not an intermediary in the formation of the peroxide. In form and in behavior this peroxide most nearly resembles the monohydroxy dialkyl peroxides which are obtained by the addition of alkyl hydroperoxides to aldehydes.[4] In the case under consideration this mode of formation would be represented by the equation



$$C_6H_5CHO + H{-}O{-}O{-}\underset{\diagdown O \diagup}{CH{-}C}(C_6H_5)_2 \longrightarrow C_6H_5{-}\underset{\underset{OH}{|}}{CH}{-}O{-}O{-}\underset{\diagdown O \diagup}{CH{-}C}(C_6H_5)_2$$

Here the intermediary is a derivative of hydrogen peroxide which could not be formed under the conditions of the experiment.

There remains only the possibility that benzoperacid does not represent the primary oxidation product of benzaldehyde. This possibility has often been discussed in connection with observations that newly oxidized benzaldehyde is a more powerful oxidizing agent than benzoperacid[6] but no positive evidence of such a product has hitherto been obtained. It seems not improbable, however, that oxidation of a concentrated solution of the oxide in benzaldehyde, or of the intimate mixture of the aldehyde and the oxide that would be formed by cleavage on the surface of the solid oxido alcohol, would present an unusually favorable condition for catching some of the moloxide before its rearrangement to the peracid. Such an energetic, neutral antecedent of the peracid would account both for the peroxide and for the other oxidation products that are always formed at the same time



$$\begin{array}{l} C_6H_5CHO.O_2 + \underset{\diagdown O \diagup}{CH_2{-}C}(C_6H_5)_2 \longrightarrow C_6H_5\underset{\underset{OH}{|}}{CH}{-}O{-}O{-}\underset{\diagdown O \diagup}{CH{-}C}(C_6H_5)_2 \\ \quad\downarrow \\ C_6H_5CO_3H + \underset{\diagdown O \diagup}{CH_2{-}C}(C_6H_5)_2 \longrightarrow (C_6H_5)_2CO + HCO_2H + \underset{\underset{OH}{|}}{CH_2}{-}\underset{\underset{OCOC_6H_5}{|}}{C}(C_6H_5)_2 + C_6H_5COOH \end{array}$$

Experimental

All the oxide used in the investigation was isolated and purified in the same manner. It was prepared in quantity as directed in the earlier paper and left in the alkaline solu-

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[3] Smit, *Rec. trav. chim.*, *49*, 676 (1930).

[4] Rieche, *Ber.*, 63,2642 (1930).

[5] (a) Engler and Weissberg, "Kritische Studien über die Vorgangen der Autoxidation," 1904, p. 91; (b) Baeyer and Villiger, *Ber.*, 33, 1569 (1900); (c) Staudinger, *ibid.*, 46, 3530 (1913); (d) Jorissen and Van der Beek, *Rec. trav. chim.*, *46*, 42 (1927); (e) Milas, *J. Phys. Chem.*, 33,1204 (1929).

tion until it was needed. A suitable quantity was then precipitated with ice water. rapidly washed and dried, and recrystallized from ether and petroleum ether.

Oxidation.—For the purpose of determining all the products of oxidation, three lots of 5 *g.* each were exposed to the air in thin layers at the bottom of large Erlenmeyer flasks until the odor of benzaldehyde had disappeared completely. The average gain in weight was 6.2%. The resulting solids were cooled in a freezing mixture and washed, repeatedly, with small quantities of equally cold ether, which removed about 20% of the material. From the ethereai solution sodium bicarbonate extracted formic acid—recognized by its reducing action on mercuric oxide—and benzoic acid which was identified in the usual manner. The ethereal layer, on distillation, left an oil which solidified almost completely when it was inoculated with benzophenone, and which formed a phenylhydrazone melting at 137°. The ethereal extract therefore contained formic acid, benzoic acid and benzophenone.

The solid was recrystallized from acetone and ether; it contained two substances: the peroxide which had been obtained before in the same manner and a small quantity of another compound which crystallized in needles and melted at 156°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.0; H. 5.8.

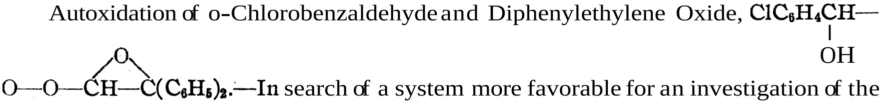
This substance is the monobenzoate of diphenyl glycol which was first obtained by Bodendorf by oxidizing diphenylethylene oxide with benzoperacid. Bodendorf assumed, perhaps correctly, that the peracid first combines with the oxide to form the corresponding perbenzoate, and that this substance is subsequently reduced to the benzoate. But the course of the reaction may be quite different because the benzoate is also formed very readily by simply dissolving benzoic acid in the melted oxide. The ratio between the amounts of peroxide and other oxidation products was not constant, the yields of peroxide varying between 70 and 80%.

Conditions Essential for the Formation of the Peroxide.—In a search for conditions more favorable for investigating the mechanism of the oxidation we passed air for twenty-four hours through neutral solutions of the oxide in alcohol, ether, acetone and benzene, but in no case obtained any oxidation. In faintly acid solutions there was a very slow oxidation but no peroxide was formed; after seventy-two hours, benzoic and diphenylacetic acids were the only oxidation products which could be detected.

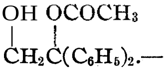
In order to ascertain the importance of acid, three portions of the same preparation of the oxide were placed in large vacuum desiccators which were first exhausted, then filled—the one with air that had been passed through very dilute ammonia, the second with air which had been passed through sodium hydroxide—and the third with air that had been passed first through sodium hydroxide and then through moderately dilute hydrochloric acid. After five days only the third sample had been oxidized, the crystals of the first and second still retaining both their shape and their luster.

Autoxidation of the Cleavage Products.—A large number of solutions of diphenylethylene oxide in benzaldehyde were oxidized both in air and in oxygen. Peroxide was formed in every experiment but in many cases the amount was small and we failed to find any conditions under which the yield was equal to that which had been obtained from the oxido alcohol. Thus, in a typical experiment a solution of 2.5 g. of diphenylethylene oxide in 1.4 g. of benzaldehyde was exposed to the air in a large Erlenmeyer flask. After five hours solid began to appear and after two days the odor of benzaldehyde had disappeared completely. The resulting solid, manipulated like the product from the oxido alcohol yielded 1.8 g. of peroxide, 0.76 g. of the monobenzoate of diphenyl glycol and smaller quantities of benzoic acid and benzophenone.

Oxidation of the Cleavage Products with Benzoperacid.—A solution of the sodium salt of benzoperacid, prepared by the method of Smit, was acidified in a dropping funnel which was surrounded with ice water. At intervals small quantities of the resulting liquid acid were drawn into a solution of *2.5* g. of diphenylethylenc oxide in **1.4** g. of benzaldehyde which was likewise cooled with ice water and which was kept in an atmosphere of nitrogen. After twenty-four hours the mixture was a solid free from benzaldehyde. By the usual manipulation, this solid yielded the monobenzoate of diphenyl glycol, benzoic acid and benzophenone, but no peroxide could be detected.

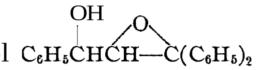
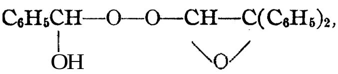

Autoxidation of o-Chlorobenzaldehyde and Diphenylethylene Oxide, $\underset{\textstyle OH}{ClC_6H_4CH}—O—O—\overset{O}{CH—C}(C_6H_5)_2$.—In search of a system more favorable for an investigation of the mechanism of autoxidation, we examined the behavior of solutions of diphenylethylene oxide in a few other aldehydes. A solution of *2* g. of the oxide in **1.5** g. of *o*-**chlorobenzaldehyde** remained liquid after exposure to the air for several days, but solidiied in the course of a week. After extraction with ether, there remained 0.9 g. of **a** solid which decomposed briskly at the melting point. This solid was recrystallized from acetone and ether from which it separated in very thin needles melting at **140–141°** with evolution of gas.

Anal. Calcd. for $C_{21}H_{17}O_4Cl$: C, **68.4;** H, 4.7. Found: C, **68.1;** H, **4.8.**


Autoxidation of Acetaldehyde and Diphenylethylene Oxide, $\underset{}{\overset{OH}{CH_2}}\overset{OCOCH_3}{C}(C_6H_5)_2$.—Various solutions of diphenylethylene oxide in acetaldehyde were exposed to the air until they had solidified completely. No peroxide could be detected in any of them; the principal product in every case was the monoacetate of diphenyl glycol, which separates from ether and petroleum ether in large prismatic crystals, and melts at **91°**.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, **6.2.** Found: C, **74.8;** H, **6.6.**

Summary


The autoxidation of the oxido alcohol $C_6H_5\overset{OH}{CH}\overset{O}{CH—C}(C_6H_5)_2$ to the peroxide $C_6H_5\underset{OH}{CH}—O—O—\underset{O}{CH—C}(C_6H_5)_2$, in all probability involves first cleavage

to benzaldehyde and diphenylethylene oxide, then autoxidation of the benzaldehyde, and finally synthesis of the peroxide from the autoxidation product of the aldehyde and diphenylethylene oxide. The intermediate in this synthesis is not benzoperacid; it appears to be an unstable "moloxide" antecedent to the peracid.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Diarsyls. IV. The Interaction of Diphenyldiiododiarsyl with Alkali, with Phenylarsine and with Diphenylarsine[1]

BY F. F. BLICKE AND L. D. POWERS

It seemed that diphenyldihydroxydiarsyl, a substance which has never been described, should be produced from the interaction of diphenyldiiododiarsyl[2] and alkali

$$C_6H_5(I)As—As(I)C_6H_5 + 2NaOH = C_6H_5(OH)As—As(OH)C_6H_5 + 2NaI$$

Diphenyldiiododiarsyl, suspended in ether, was shaken with excess sodium hydroxide solution in a free radical apparatus filled with nitrogen. The halogen was removed rapidly and quantitatively from the diarsyl and a crystalline, alkali-insoluble material remained partly dissolved and partly suspended in the ether layer. Upon separation and acidification of the alkaline solution a considerable amount of phenylarsine oxide was obtained. The alkali-insoluble product, after it had been recrystallized twice from benzene, possessed properties which in some respects resembled those of arsenobenzene; in certain other characteristics, however, the material was decidedly dissimilar to this substance as is shown by the following tabulation.

ALKALI-INSOLUBLE PRODUCT	ARSENOBENZENE
Separates from a benzene solution in the form of large, granular crystals	Separates from a benzene solution in the form of fine needles
M. p. 195–197°.[a] Mixed with arsenobenzene, m. p. 190–195°[b]	M. p. 210–212°
Mol. wt., 603[c]	Mol. wt. 867;[d] calcd. 304
% As, 47.12[e]	% As, 49.31
Absorbs oxygen rapidly[f]	Does not absorb oxygen
Dissolves rapidly in ether upon the addition of HCl or HBr; arsenobenzene precipitates quickly from the solution	Does not dissolve in ether upon the addition of a halogen acid
One hundred cubic centimeters of boiling benzene dissolve 7.9 g. of the material	One hundred cubic centimeters of boiling benzene dissolve 1.4 g. of this compound
Yields diphenyldiiododiarsyl when treated with iodine in ether	Yields diphenyldiiododiarsyl when treated with iodine in ether

[a,b] The melting point was determined in a sealed tube filled with nitrogen. [c] This result represents the average of six determinations on three different samples of material. The determinations were made in boiling benzene in a stream of nitrogen. [d] This value was obtained in boiling benzene in a stream of nitrogen; previously the molecular weight had been found to be 895 and 915, under the same experimental conditions [Blicke and Smith, THIS JOURNAL, 52, 2950 (1930)]. [e] This figure represents the average value of six analyses made with three different samples of material. [f] 1.042 g. of the product absorbed 73 cc. (N. T. P.) of oxygen in five minutes.

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(1) This paper represents the second part of a dissertation submitted to the Graduate School by L. D. Powers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Blicke and Smith, THIS JOURNAL, 52, 2937 (1930).

Diphenyldibromodiarsyl, when hydrolyzed, yielded products identical with those obtained from diphenyldiiododiarsyl. Di-*p*-anisyldiiododiarsyl yielded panisylarsine oxide and an alkali-insoluble compound which, to some extent, resembled di-*p*-methoxyarsenobenzene, yet seemed to be different from this material.

It has been claimed by Steinkopf and Smie[3] that diphenyldiiododiarsyl, suspended in alcohol, reacts with diphenylarsine at 70" to form hexaphenyltetraarsine $(C_6H_5)_2As—As(C_6H_5)—As(C_6H_5)—As(C_6H_5)_2$. The only experimental fact offered in support of this structure was an arsenic analysis, which differed from the calculated amount of arsenic by 2.98%, and the behavior of the material with iodine; in the latter reaction phenyldiiodoarsine and diphenyliodiarsine were formed in approximately equivalent amounts. No melting point was recorded and the above mentioned investigators admitted that their product was impure.

We have found that the compounds under discussion react at ordinary temperature in an entirely different manner, namely, with the formation of tetraphenyldiarsyl and arsenobenzene. Such a mixture would, of course, contain the same amount of arsenic as hexaphenyltetraarsine and, upon treatment with iodine, would yield phenyldiiodoarsine and diphenyliodoarsine in equivalent amounts. It seems very probable that the tetraarsine of Steinkopf and Smie was, in reality, a mixture of tetraphenyldiarsyl and arsenobenzene.

$$C_6H_5(I)As—As(I)C_6H_5 + 2(C_6H_5)_2AsH = (C_6H_5)_2As—As(C_6H_5)_2 + C_6H_5As{=}AsC_6H_5 + 2HI$$

Diphenyldiiododiarsyl and phenylarsine react to form arsenobenzene.

$$2C_6H_5(I)As—As(I)C_6H_5 + 2C_6H_5AsH_2 = 3C_6H_5As{=}AsC_6H_5 + 4HI$$

Steinkopf and Smie[3] stated that these compounds yield cyclic triphenyltriarsine, $C_6H_5As—As(C_6H_5)—AsC_6H_5$, but since no melting point was reported for the triarsine and the calculated analytical data for this compound are the same *as* for arsenobenzene, the alleged formation of the triarsine in this reaction seems to have been based on an insufficient amount of experimental evidence.

Experimental Part

Hydrolysis of **Diphenyldi-iododiarsyl.**—The diiododiarsyl was prepared from 24.4 g. of **phenyldiiodoarsine,**[4] 50 cc. of absolute alcohol and 40 g. of crystalline phosphorous acid, dissolved in 200 cc. of alcohol. The diarsyl was then suspended in 100 cc. of ether, shaken for one hour with 100 cc. of 10% sodium hydroxide solution, the alkaline layer decanted and the ether layer extracted three times with 50-cc. portions of alkali. Upon neutralization of the alkaline extracts with sulfuric acid in a nitrogen atmosphere,

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(3) Steinkopf and Smie, Ber., 69, 1462 (1926).

(4) This material, after it has been preserved for some time in a glass-stoppered bottle, becomes very dark in color and often contains a considerable amount of a crystalline product. The iodide, however, seems to undergo little, if any, decomposition if it is kept under a layer of concd. hydriodic acid.

3.8 g. of phenylarsine oxide was obtained, mixed m. p. 145–147°,[5] after recrystallization from benzene–ether.

The ether layer, which contained suspended material, was concentrated to a volume of 15 cc. and the liquid decanted. The latter possessed a very strong odor similar to that of phenylarsine. The slightly yellow crystalline material was washed with alcohol, then with ether and dried under diminished pressure. After a second recrystallization from benzene the product, which was halogen free, weighed 3.2 g.

When 2.06 g. of the material, suspended in 50 cc. of ether, was shaken with 25 cc. of hydrobromic acid 1.13 g. of arsenobenzene, m. p. 210–212°, was obtained.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.26.

From 1.72 *g.* of the product, 50 cc. of ether and 1.4 g. of iodine there was produced 1.45 g. of diphenyldiiododiarsyl; m. p. 177–178°.

Hydrolysis of Di-*p*-anisyldiiododiarsyl.—When the diiododiarsyl,[6] obtained from 13.1 g. of *p*-anisyldiiodoarsine,[7] was hydrolyzed in the manner described above, there was obtained 2.5 *g.* of p-anisylarsine oxide, m. p. 136–138°, and 1.7 g. of a crystalline halogen-free, alkali-insoluble product, m. p. 220-230": % As found, 40.02 and 40.20.

Dissolved in bromobenzene 1.082 g. of the alkali-insoluble product absorbed 61 cc. of oxygen in two minutes.

When the alkali-insoluble material was suspended in ether and treated with hydrochloric or hydrobromic acid di-@-methoxyarsenobenzenewas obtained; mixed m p. 233–235°.[8]

Phenylarsine and Diphenyldi-iododiarsyl.[9]—To 6.79 g. (0.012) mole of diphenyldiiododiarsyl, suspended in 75 cc. of absolute alcohol, there was added 2.4 g. (1.8 cc., 0.015 mole) of phenylarsine. After the mixture had been shaken for twelve hours the deep yellow color of the diiododiarsyl had disappeared and a pale yellow compound remained suspended in the solvent. The alcohol was decanted, the solid material washed with alcohol and ether and then dried for some time in the radical bulb under diminished pressure. This material melted from 140–212° and absorbed oxygen: 0.600 *g.* absorbed 11 cc. in two minutes. The smallest possible amount of boiling xylene necessary to dissolve the product was introduced into the radical bulb; after two days 2.8 g. of pure arsenobenzene had separated from the solution; mixed m. p. 209–210°; calcd. yield 5.5 g.[10]

Anal. Calcd. for $C_{12}H_{10}O_2$: As, 49.31. Found: As, 49.07.

When alcohol was replaced by absolute ether in the above experiment and the mixture shaken for three days, 87% of the diiododiarsyl was recovered unchanged.

Diphenylarsine and Diphenyldiiododiarsyl.—The diphenyldiiododiarsyl, obtained from 8.12 g. (0.02 mole) of phenyldiiodoarsine, 14 g. of crystalline phosphorous acid and 100 cc of absolute alcohol—approximately 0.01 mole[11]—was suspended in 60

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[5] For further identification the oxide was converted into phenyldichloroarsine and the latter identified as phenylarsplene N-pentamethylenedithiocarbamate [Blicke and Oakdale, THIS JOURNAL, **54, 2995 (1932).** The melting point of this compound should be 183–184° instead of 173–174° as recorded previously.

[6] Blicke and Smith, ibid., 52, **2043 (1930).**

[7] Blicke, Powers and Webster, *ibid.*, **54, 2946 (1932)**

[8] A sample of di-p-methoxyarsenobenzene, obtained by reduction of p-anisylarsine oxide in acetic acid with hypophosphorous acid, melted at 228–230° after recrystallization from bromobenzene.

[9] A description of the apparatus used in this and the following experiment was published previously [Blicke and Powers, ibid., 54, **3356** (1932)].

[10] The yield was, undoubtedly, lowered to a decided extent by recrystallization. In the recrystallization of pure arsenobenzene from xylene the yield of crystalline product which separated from the xylene was about **50%;** only gummy material could be obtained from the mother liquor.

[11] The diiododiarsyl was not removed from the free radical bulb in which it had been prepared. In a number of instances in which the diarsyl, prepared by this method, had been isolated the yield of pure product was never less than 90% of the calcd. amount.

cc. of absolute alcohol and 4.60 g. (3.54 cc., 0.02 mole) of diphenylarsine added.[12] The mixture, initially yellow in color, was shaken vigorously for twelve hours; after thirty minutes it had become colorless. The alcohol was decanted from the solid material into a second radical bulb and the alcohol removed by distillation under reduced pressure. In order to separate the compounds formed, arsenobenzene and tetraphenyldiarsyl, advantage was taken of the fact that the latter substance is soluble in ether while arsenobenzene is practically insoluble in this solvent. One hundred cubic centimeters of ether was poured onto the mixture, whereupon most of the tetraphenyldiarsyl dissolved. The ether solution was then decanted through a Jena filter into the second bulb. The purpose of the filter was to retain finely divided arsenobenzene which remained suspended in the ether. The arsenobenzene was washed with ether until free from the diarsyl. The residue of arsenobenzene weighed 2.97 g.; m. p. 203–207"; calcd. yield 3.04. After recrystallization from bromobenzene it melted at 208–210°.

The ether solution in the second bulb was shaken with alkali to remove traces of unchanged iodides, washed free from alkali and then concentrated to a volume of 25 cc.; a copious precipitate of tetraphenyldiarsyl was obtained. After recrystallization from absolute alcohol, the material weighed 2.6 g., m. p. 128–130°.[13] Upon concentration of the mother liquor an additional 0.4 g. of product was obtained; calcd. yield 4.58 g.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As. 32.72, 32.69.

Summary

Several diaryldihalodiarsyls were treated with alkali whereupon an arylarsine oxide and an alkali-insoluble product were formed.

Phenylarsine and diphenyldiiododiarsyl react to form arsenobenzene; diphenylarsine and the diiododiarsyl yield arsenobenzene and tetraphenyldiarsyl. It has been claimed in the literature, on the basis of meager experimental data, that cyclic triphenyltriarsine is formed in the first instance and hexaphenyltetraarsine in the second.

ANN ARBOR, MICHIGAN

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[12] No reaction seemed to take place when ether was used as *a* solvent.

[13] Blicke. Weinkauff and Hargreaves, THIS JOURNAL, 52, 782 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BIRMINGHAM-SOUTHERN COLLEGE]

The Structure of X-Chlororesorcinol

BY BENJAMIN F. CLARK

In a recent investigation, the author obtained a considerable quantity of a material which corresponded in all its characteristics with the compound listed in Beilstein as "x-chlororesorcinol." This material was first prepared by Reinhard,[1] who obtained it by treating resorcinol with sulfuryl chloride. In an attempt to determine the structure of this compound, Reinhard endeavored to replace the chlorine atom with a hydroxyl group by fusion of the compound with sodium hydroxide and also potassium hydroxide, but he obtained no trihydroxybenzene, even when he heated the materials as high as 250°. Heating above 250" caused charring to take place.

The author attempted to convert chlororesorcinol into the corresponding trichlorobenzene by prolonged heating with phosphorus pentachloride. A sample of chlororesorcinol, even when heated for eight hours at 250" with phosphorus pentachloride, gave only a rubber-like residue from which no material resembling any of the trichlorobenzenes could be extracted. When a temperature lower than 250" was used, no reaction took place.

It seemed likely that the chlorine atom was in the ortho position with respect to one hydroxyl group and para with respect to the other; accordingly, a synthetic method for making this compound was devised. The physical constants of the material obtained, as well as those of several of its derivatives, were then found and compared with those obtained by Reinhard with his "x-chlororesorcinol."

Chlorobenzene was chosen as the starting point, and from it 2,4-dinitrochlorobenzene was prepared. The nitro compound was then reduced to the corresponding amine, 2,4-diaminochlorobenzene. The physical constants for these materials compared closely with those recorded in the literature, The amino compound was diazotized and the diazonium groups then replaced by hydroxyl groups.

Experimental

2,4-Dinitrochlorobenzene.—The method of Einhorn and Fry[2] was used in the preparation of this compound, m. p. 49.5° **(corr.)** from alcohol.

2,4-Diaminochlorobenzene.—For the reduction of the nitro compound, the method of Beilstein and Kurbatow was used, m. p. 90–91° **(corr.)** from **alcohol.**[3]

Chlororesorcinol.—20.0 grams (0.140 mole) of 2,4-diaminochlorobenzene was dissolved in 500 cc. of 10% hydrochloric acid, to which had been added 200 **g.** of cracked

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[1] Reinhard, J. *prakt.* Chem., [11]17,322 (1878).

[2] Einhorn and Fry, ***Ber.***, 27,2457 (1894).

[3] Beilstein and Kurbatow, **I.** Russ. *Phys.-Chem. Soc.*, 11,370 (1879).

ice; 19.5 g. (0.280 mole) of C. P. sodium nitrite, dissolved in 200 cc. of water, was slowly added and the solution stirred constantly. The solution was then allowed to come slowly to room temperature. After standing overnight, the solution was distilled with steam. Nitrogen was evolved and a cream-colored crystalline material appeared in the distillate. When no more crystals came over, the distillate was filtered and the crystals carefully dried on a porous plate; yield 15.2 g. (96%). The crude material melted at 87–87.5°, and after two recrystallizations from alcohol it melted at 88.5–89.0° (corr.). Reinhard obtained a melting point of 89° for "x-chlororesorcinol." A mixed melting point determination, made on a portion of the material mixed with a sample of chlororesorcinol made by Reinhard's method, gave a value of 88.5–89.0°.

The bromine derivative, prepared according to Reinhard's method, melted at 103.5–104.0°, after one recrystallization from alcohol. Reinhard obtained a melting point of 105° for this compound.

The dibenzoyl derivative melted at 97° as compared with the value of 98° reported by Reinhard.

Analysis of the purified chlororesorcinol, as obtained by the above method, gave the following results: calcd., Cl, 24.53; found, Cl, 24.63. The method of Lemp and Broderson[4] was used in this analysis.

Conclusion

As a result of a synthetic method, in which chlororesorcinol was prepared from compounds of known structure, it has been shown that "x-chlororesorcinol" has the structure 1-chloro-2,4-dihydroxybenzene.

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[4] Lemp and Broderson, THIS JOURNAL, 39, 2069 (1917).

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[CONTRIBUTION FROM THE RUSSELL-MILLER MILLING CO. LABORATORY]

Lipases of Wheat. I

BY B. SULLIVAN AND M. ALLISON HOWE

No studies of any of the lipases of wheat or its products have been reported in the literature. Furthermore, no references have been made concerning the importance of lipase in relation to the quality and storage of wheat products. Therefore considerable preliminary work is necessary in establishing the following fundamental facts (a) the most reliable method for the measurement of the lipase activity of wheat; (b) the best methods of extraction to increase the concentration of the enzyme from any given wheat product; (c) the distribution of the enzyme in the different milling separations of wheat; (d) the optimum conditions of time, temperature and PH for wheat lipase activity as well as the specificity of different buffer mixtures, the effect of various activators and inhibitors and the action of the enzyme on various substrates. These preliminary experiments described here are intended to establish some of the variables influencing the activity of the lipases of wheat and its products.

Experimental

An arbitrary method of measuring the lipase activity was first developed based on a number of different methods previously reported in the literature. Ground wheat was used as the source of the enzyme. The method used was as follows: 0.5 g. of finely ground wheat was incubated for twenty-four hours at 37.9° in a 250-cc. Erlenmeyer flask with 10 cc. of water, 2 cc. of toluene, the substrate (1 cc. of liquid or 1 g. of solid fat) and 10 cc. of buffer solution. At the end of the incubation period, 100 cc. of 3:1 acetone–ether mixture was added to the sample and also the blank which had been boiled previous to incubation; 0.1 *N* sodium hydroxide was used for the titration with 1% phenolphthalein as an indicator. The results obtained from various substrates are given in Table I. The action of the enzyme was tried in the alkaline and also in the acid range on all the substrates used. It will be noted that in the case of the liquid triglycerides of the saturated fatty acids, the titration value decreases with an increase in molecular weight. Since a few of these substrates are solids, there would be less surface than in the case of the liquids and this would affect the rate of enzyme action. It is generally assumed that wheat germ which has the highest fat content of all the milling separations also has the highest lipolytic activity. However, in comparing all the milling separations, other fractions showed greater activity in the hydrolysis of certain neutral triglycerides. The PH of the boiled preparation including the sample, substrate, toluene and buffers was determined potentiometrically in all cases. Since phosphates are the natural buffers of wheat, it was desirable to use phosphate buffers wherever possible. Mixtures of primary potassium phosphate and secondary sodium phosphate were employed for one group of determinations, and primary potassium phosphate and borax for the more alkaline range. Graphs I and II show the results obtained. In Table II, the results are given of various methods tried in an effort to increase the activity of the enzyme. None of these methods was found to

TABLE I

ACTION OF LIPASE IN WHEAT PRODUCTS ON VARIOUS SUBSTRATES EXPRESSED IN CC. OF *N*/10 SODIUM HYDROXIDE

Clear																	
Triacetin		Tri-propionin		Tributyrin		Tri-*n*-valerin		Tricaproin		Tri-caprylin		Trimyristin		Tri-palmitin		Tristearin	
PH	Cc.	*PH*	Cc.	*PH*	Cc.	PH	Cc.	*PH*	Cc.	*PH*	Cc.	*Pa*	Cc.	*PH*	Cc.	PH	Cc.
7.6	31.4	7.4	13.7	7.1	1.8	7.6	0.4	7.3	0.3	7.6	0.2	7.6	0.2	7.6	0.5	7.6	0.2
7.4	28.8	6.7	13.1	6.7	2.0	7.4	0.6	6.7	0.5	7.4	0.4	7.4	0.4	7.4	0.9	7.4	0.3
5.2	14.7	4.7	8.4	4.7	2.6	5.2	1.6	4.7	1.4	5.2	0.7	5.2	1.4	5.2	1.6	5.2	1.2

Clear						Wheat			
PH	Ethyl propionate	Ethyl butyrate	Ethyl stearate	Ethyl oleate	Olive oil	*PH*	Triacetin	Tri-stearin	Ethyl acetate
7.6	1.1	0.2	0.6	0.7	0.4	7.5	27.8	0.4	8.4
7.4	1.7	0.5	0.4	1.6	0.6	6.3	20.3	...	6.9
5.2	3.0	1.9	0.3	1.8	1.7	5.8	16.0	0.6	6.0
						5.2	12.6	1.3	5.9

give more than a very slight increase in the titration value over that obtained on the untreated and unextracted sample when using triacetin as the substrate. When germinated wheat was used with some of the higher triglycerides, an increased action was observed. As these higher triglycerides are the natural components of wheat, further work is to be done on the higher fats.

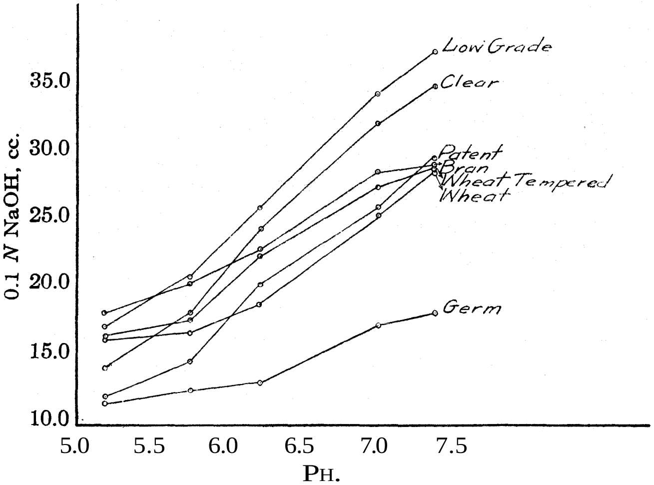

Fig. 1.—Buffers: KH_2PO_4 and $Na_2HPO_4 \cdot 12H_2O$.

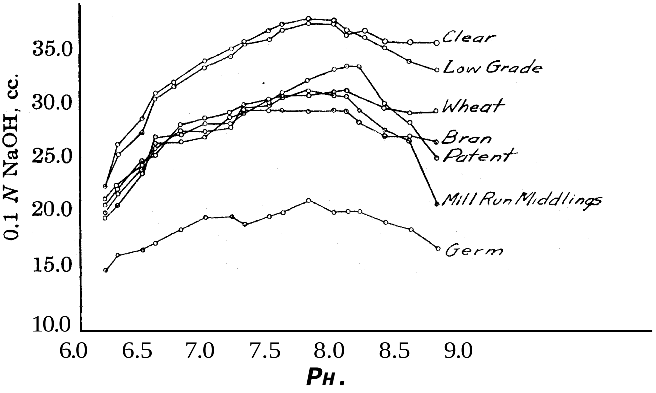

Fig. 2.—Buffers: 0.1 M KH_2PO_4 and 0.5 *M* $Na_2B_4O_7 \cdot 10H_4O$.

A comparison was made using *Ricinus* lipase and the lipase of soy bean prepared by exhaustive ether extraction of the beans. Neither of these preparations gave as high results as the ground untreated wheat when triacetin was used as a substrate.

A negative test for the free amino group was obtained by testing the in-

TABLE II

GROUND WHEAT EXTRACTED BY VARIOUS METHODS IN AN EFFORT TO INCREASE THE CONCENTRATION OF THE LIPASE WHICH ACTS ON TRIACETIN

Results Expressed in Cc of $N/10$ Sodium Hydroxide

PH	Resting wheat not extracted	Exhaustive ether extraction	Exhaustive toluene extraction	Germinated	Glycerin extraction	Water extraction filtrate	Water extraction residue
5.8 **(no buffers)**	22.1	23.1	22.6	22.5	13.6	8.4	7.1
7.7	27.4	29.0	28.0	29.0	19.7	17.9	10.1
7.4	25.9	27.0	25.9	27.5	19.7	16.9	9.2
6.3	20.1	21.8	21.3	22.0	..	12.6	7.8
5.8	17.9	17.6	17.5	18.4	..	8.9	6.3
5.3	14.4	12.8	14.6	16.5	..	6.8	3.8

PH	Preliminary Digestion with Trypsin: Residue extracted with ether	Preliminary Digestion with Trypsin: Residue not extracted with ether	Preliminary Digestion with Trypsin: Filtrate from tryptic digestion	Preliminary Digestion with Diastase: Residue extracted with ether	Preliminary Digestion with Diastase: Filtrate
5.8 (no buffers)	3.1	2.5	19.5	3.1	13.5
7.7	4.2	2.9	24.1	3.0	19.1
7.4	3.1	3.1	23.5	4.0	19.0
6.3	4.0	4.5	..	4.0	..
5.8	3.3	3.2	..	3.7	..
5.2	2.0	2.5	..	3.2	..

PH		Trimyristin	Tripalmitin	Tristearin	Wheat fat E. E.
	Unextracted wheat				
5.2	**Germinated (three days)**	**3.2**	2.6	1.8	2.2
5.2	**Resting**	1.5	0.7	0.4	0.7
	Ether extracted wheat				
5.2	**Germinated previous to extraction**	...	...	...	2.2
5 2	**Resting**	...	...	...	1.1

cubated products with ninhydrine, eliminating the possibility of any increase in titratable acidity being due to amino acids.

Discussion

Glycerides of the lower fatty acids, particularly triacetin and tripropionin, were acted on to the greatest extent, triacetin giving considerably higher results than any other substrate tried. Ethyl acetate gave a higher titration value than ethyl butyrate, which showed very little action, although neither of these esters was acted on to the extent of triacetin and tripropionin. This fat splitting enzyme of wheat acts on the glycerides of the fatty acids to a greater extent than on the corresponding esters. The higher titration values given by triacetin and ethyl acetate compared to the higher members of their series is, however, undoubtedly purely physical and is probably due to the relatively greater water solubility of these lower members. No triolein or glycerides of other unsaturated fatty acids were tried in these experiments, although olive oil was found to give a titration value comparable to the higher saturated glycerides. With olive oil as a substrate, the enzyme has its optimum P_H in the acid range. Many investigators in this field have measured the extent of lipase activity by the use of triacetin, tributyrin, ethyl butyrate and such compounds of the lower fatty acids as substrates. Since the higher fatty acids, such as stearic, palmitic and oleic, are those commonly present in plant and animal tissues, it would seem to the authors that lipase studies to be of any practical significance should be directed toward the use of such substrates as are present in greatest amounts in natural products.

This study is being continued in an effort to find the optimum conditions of time, temperature and P_H under which the higher triglycerides, lecithin and other lipides naturally present in wheat are hydrolyzed. An effort is being made to obtain a more active enzyme preparation by other methods than those already described and to study the effect of various activators and inhibitors on such preparations.

The authors wish to thank Dr. G. O. Burr and Dr. W. M. Sandstrom for valuable suggestions.

Summary

1. A method has been described for the measurement of the activity of the lipase of wheat products and it has been shown that with the time and temperature employed, and with triacetin as the substrate, the enzyme was most active on the alkaline side at P_H 7.3 to 8.2 and that it has a wide optimum range. All wheat products show a marked action in cleaving triacetin, the highest values being given by low grade flour rather than by germ or bran. When the higher triglycerides of fatty acids naturally present in wheat were used as substrates, the enzyme showed an optimum on the acid side. Germination of wheat increased the activity of its lipase when the higher triglycerides were used as substrates, but made very little difference when triacetin and the glycerides of the lower fatty acids were employed.

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[CONTRIBUTION FROM THE NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

Condensations of Isatin with Acetone by the Knoevenagel Method[1]

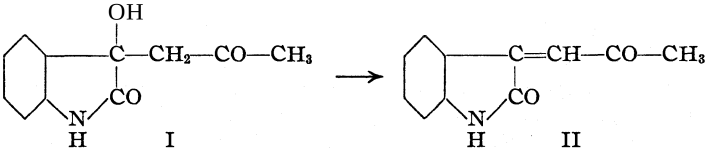
BY F. BRAUDE WITH H. G. LINDWALL

In a recent article it was shown[2] that isatin and acetophenone will condense, in the presence of certain bases, to yield 3-hydroxy-3-phenacyloxindole. This reaction suggested the use of other methyl ketones like acetone. Isatin and acetone condense when present with small amounts of diethylamine to yield 3-acetonyl-3-hydroxyoxindole (I).

The condensation involves the β-carbonyl of the isatin molecule rather than the nitrogen, for N-methylisatin will also react with acetone to yield a product with chemical properties similar to those of (I).

Compound (I) decomposes upon the application of heat, or upon being warmed with aqueous alcoholic potassium hydroxide solution, into isatin and acetone. This decomposition is evidently another example of a reversed aldol reaction. A longer period of heating with the potassium hydroxide solution results in the formation of 2-methylcinchoninic acid, not, apparently, through rearrangement of the 3-acetonyl-3-hydroxyoxindole, but rather through its decomposition into isatin and acetone followed by a Pfitzinger[3] type of condensation of the acetone with the *o*-aminobenzoylformic acid, formed by the hydrolysis of the isatin.

Treatment of I with certain acidic reagents effects the loss of one mole of water with the resulting formation of 3-acetonylideneoxindole (11), a highly colored red-orange compound.



I II

It might be expected that II, upon ring opening through hydrolysis, would form 2-methylcinchoninic acid as a result of subsequent reaction of the ketone carbonyl with the nuclear NH_2 group. However, II could not be rearranged to the corresponding quinoline derivative by treatment with potassium hydroxide. This is in agreement with the failure of 3-phenacylideneoxindole and 3-phenacyloxindole to rearrange to cinchophen and 3,4-dihydro-2-phenylcinchoninic acid, as noted in our previous paper. Therefore 3-acetonylideneoxindole cannot, apparently, be considered an intermediate in the Pfitzinger synthesis of 2-methylcinchoninic acid from isatin

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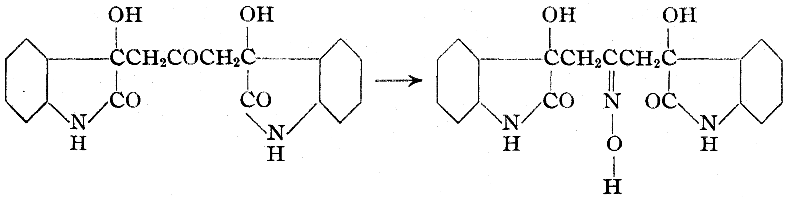
[1] Abstract from a thesis presented by F. Braude in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Lindwall and Maclennan, THIS JOURNAL, 54, 4739 (1932).

[3] Pfitzinger, J. *prakt.* Chem., 33, 100 (1886); 38, 583 (1888); 56, 283 (1897).

and acetone. It is possible that II is a *trans* isomer and will not form the quinoline derivative for this reason. This point has not yet been completely investigated.

3-Acetonyl-3-hydroxyoxindole will condense with a mole of isatin to yield 1,3-bis-(3-hydroxy-3-oxindyl)-2-propanone (III). This compound also results when 2 moles of isatin condense with one of acetone. N-Methylisatin behaves in an analogous manner with acetone. Compound III yields a monoxime (IV)



III IV

Experimental Part

3-Acetonyl-3-hydroxyoxindole (I).—A mixture of 25 g. of isatin, 139 g. of acetone and 13.9 g. of diethylamine was allowed to stand for twenty-four hours at room temperature. Pale yellow crystals separated which became white upon recrystallization from acetone. The product is soluble in ethyl alcohol, n-butyl alcohol, acetone and ethyl acetate, but is insoluble in water; m. p. 166–167° with decomposition; yield, 75%.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.62; H, 5.44; N, 6.83. Found: C, 64.48; H, 5.42; N, 6.82.

3-Acetonyl-3-hydroxy-1-methyloxindole.—The same proportions and procedure were used as for I (above), replacing the isatin by N-methylisatin The product was recrystallized from benzene: m. p. 145°; yield, 79%.

Anal. Calcd. for $C_{12}H_{13}O_3N$: N. 6.39. Found: N, 6.28, 6.31.

Isatin by the Decomposition of 3-Acetonyl-3-hydroxyoxindole (I).—A mixture of 2 g. of (I), 22.5 cc. of ethyl alcohol and 10.5 cc. of 33% potassium hydroxide was heated on a steam-bath for one hour. The resulting solution was acidified with dilute hydrochloric acid. A brown precipitate resulted which proved, upon crystallization, to be isatin; m. p. 198°; m. p. mixed with a known sample of isatin, 198°.

2-Methylcinchoninic Acid from **3-Acetonyl-3-hydroxyoxindole.—The** mixture described above was heated for eight hours on a steam-bath. Acidification with hydrochloric acid yielded a light brown precipitate. Crystallization from boiling water gave a white crystalline product which was identified, by melting point and mixed melting point, as 2-methylcinchoninic acid.

3-Acetonylideneoxindole (II).—3-Acetonyl-3-hydroxyoxindole (10 g.) was heated with 45 cc. of ethyl alcohol and 11.5 cc. of concd. hydrochloric acid until a clear solution was obtained. The solution was then poured over 80 g. of ice. A bright yellow-red solid formed. Recrystallization from ethyl alcohol yielded red needles, soluble in ether, acetone, ethyl acetate, ethyl alcohol and hot benzene: m. p. 168–171°; yield, 42%

Anal. Calcd. for $C_{11}H_9O_2N$: N, 7.49 Found: N, 7.43, 7.48.

3-Acetonylidene-1-methyloxindole.—3-Acetonyl-3-hydroxy-1-methyloxindole was treated as outlined above in the preparation of II. The product is red and soluble in alcohol and ether: m. p. 120–122"; yield, 57%.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.90; H, 5.51; N, 6.97. Found: C, 71.45; H, 5.51; N, 6.84, 7.00.

Attempted Rearrangement of 3-Acetonylideneoxindole to 2-Methylcinchoninic Acid.—A mixture containing 1.25 g. of 3-acetonylideneoxindole, 2.9 g. of sodium hydroxide and 22 cc. of water was heated on a steam-bath for eight hours. Acidification with hydrochloric acid caused the precipitation of a brown solid. Attempts to isolate 2-methylcinchoninic acid from this material were not successful.

1,3-Bis-(3-hydroxy-3-oxindyl)-2-propanone (III).—(A) A mixture of 2.9 g. (1 mol), of isatin, 4.1 g. (1 mol) of 3-acetonyl-3-hydroxyoxindole, 2.7 g. of diethylamine, and 27 cc. of absolute ethyl alcohol was allowed to stand for forty-eight hours. The solid material which separated was recrystallized from ethyl alcohol and obtained as colorless prisms: m. p. 212–214°, with apparent decomposition; yield, 78%.

(B) A solution of 4.5 g. of isatin, 1.8 g. of acetone, 2.5 g. of diethylamine, and 25 cc. of absolute alcohol was allowed to stand at room temperature for twenty-four hours. A solid formed which, after crystallization from alcohol, was found to be identical with the product from method "A"; yield, 16%.

Anal. Calcd. for $C_{19}H_{16}O_5N_2$: C, 64.76; H, 4.58; N, 7.95. Found: C, 64.54; H, 4.75; N, 7.80, 7.85.

1,3-Bis-(3-hydroxy-3-oxindyl)-2-propanone Oxime (IV).—Compound III (4.3 g.) was dissolved in 50 cc. of hot ethyl alcohol, and a water solution of 2.6 g. of hydroxylamine hydrochloride and 4.8 g. of sodium acetate was added. The solution was boiled gently for a half hour. After cooling and evaporation of solvent a solid resulted which was crystallized from 50% ethyl alcohol, and thus obtained as colorless needles, decomposing at 158–160°.

Anal. Calcd. for $C_{19}H_{17}O_5N_3$: N, 11.45. Found: N, 11.64.

1,3-Bis-(3-hydroxy-1-methyl-3-oxindyl)-2-propanone.—3-Acetonyl-3-hydroxy-1-methyloxindole and N-methylisatin were allowed to react using the procedure described in method "A" for the preparation of III. The product was recrystallized from toluene and obtained thus as colorless plates: m. p. 178–181°, with apparent decomposition.

Anal. Calcd. for $C_{21}H_{20}O_5N_2$: N, 7.39. Found: N, 7.24.

Summary

Isatin and acetone condense in the presence of certain organic bases to yield 3-acetonyl-3-hydroxyoxindole and 1,3-bis-(3-hydroxy-3-oxindyl)-2-propanone.

3-Acetonylideneoxindole is apparently not an intermediate in the Pfitzinger synthesis of 2-methylcinchoninic acid, since it does not yield that product upon treatment with alkali.

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Physico-Chemical Properties and Hypnotic Action of Substituted Barbituric Acids

BY D. L. TABERN AND E. F. SHELBERG

Henderson,[1] in a recent review, has enumerated no less than ten distinct theories that have been proposed to account for the mechanism of hypnotic action. The one which has best stood the test of time, or perhaps we should say, has developed the fewest shortcomings, is that of Meyer and Overton. This states that all chemically indifferent bodies which are soluble in fats or lipoids act as narcotics to living protoplasm; the relative degrees of activity of such narcotics depend on their affinity for fat-like substances on the one hand and for other body constituents on the other; as an approximate measure of this ratio, one may determine the distribution coefficient of the substances between oil and water.

Within the last ten years, barbiturates have come to occupy a prominent place among hypnotics, not only in routine medical practice, but in the more specialized fields of pre-anesthetic sedation and the prevention of local anesthetic reactions. These newer uses have been made possible by the development of new members possessing specifically valuable properties. For instance, certain members containing the (1-methyl butyl) group are not only the most potent yet described,[2] but are quickly broken down in the body. This leads to a period of intense hypnosis followed by rapid recovery without the prolonged depression characteristic of longer acting substances. The advantage of such rapid recovery following operative procedures is self obvious. Tatum[3] has recently shown that *n*-butylethylbarbituric acid is particularly effective in the prevention of local anesthetic intoxication.

There have now been synthesized and accurately evaluated pharmacologically more than one hundred barbiturates of relatively similar structure; over sixty have been tested in our own laboratories by a standard procedure; in addition, we have available a considerable mass of clinical data regarding prominent members. We may not only vary the number of carbon atoms in each of the alkyl groups present, but in the higher members we have many possibilities of isomerism.

It seemed of interest, therefore, to study the applicability of certain of the above-mentioned theories of hypnotic action to the barbiturates.

Of practical importance was the possibility that, if a definite relation could be established between certain physical-chemical properties and the hypnotic activities, a chemical method could be made available for the

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(1) Henderson, *Physiol. Rev.*, 10, 171 (1930). An excellent bibliography is included.

(2) Volwiler and Tabern, THIS JOURNAL, 52, 1676 (1930); Shonle, Keltch and Swanson, *ibid.*, 52, 2440 (1930).

(3) Tatum, personal communication.

preliminary evaluation of newly synthesized compounds. We have selected fifteen members, some because of their commercial importance, others because they contained interesting chemical groupings. The total length of the carbon chains attached to the "5" carbon varied from 2 to 11 atoms, covering not only the rise in hypnotic efficiency, but also its subsequent decrease in higher members. Two isomeric butyl and three isomeric amyl groups were included. Two compounds contained asymmetric carbon atoms.

Distribution coefficients of the barbituric acids were determined between water and a specially purified fatty acid free olive oil at 20°. Equal amounts of the oil and the aqueous solutions were continuously agitated for a number of hours until equilibrium had been established. Analyses of the aqueous phase were made by the Kjeldahl method.

TABLE I

No.	Barbiturate	Mol. wt.	Sol. g. per liter	Dist. coeff.. av.	Efficiency[a] rating
1	Dimethyl	156	2.419	0.066	0
2	Diethyl (Barbital)	184	6.00	.014	+
3	Ethyl i-propyl (Ipral)	198	1.36	.73	+
4	*i*-Propyl allyl	212	4.02	1.12	+++
5	Diallyl (Dial)	208	1.465	0.85	++
6	n-Butyl ethyl (Neonal)	212	1.90	2.58	+++
7	*Sec.*-butyl ethyl	212	1.987	1.36	+++
8	*Sec.*-butyl allyl	224	2.16	2.48	++++
9	*n*-Amyl ethyl	226	0.554	2.92	+++
10	*i*-Amyl ethyl (Amytal)	226	.530	2.895	+++
11	Ethyl (1-methyl butyl) (Nembutal)[b]	226	1.20	4.4	++++
12	*Sec.*-butyl β-bromoallyl (Pernocton)	304	0.684	4.3	++++
13	Phenyl ethyl (Phenobarbital)	234	.970	1.34	++
14	Allyl (methylhexylcarbinyl)	280	3.06	0.306	0
15	Ethyl (methylhexylcarbinyl)	267	0.414	.408	0

[a] Since variations of technique such as the route of administrations, etc., lead to slightly divergent numerical data, it seems most satisfactory to employ only comparative values. [b] Nembutal (pentobarbital sodium) is the sodium salt of this acid.

Table I demonstrates a definite parallelism between the partition coefficients and hypnotic efficiency, both increasing from a low value in dimethyl to a maximum in ethyl (1-methyl butyl), *sec.*-butyl allyl, and *sec.*-butyl (β-bromoallyl)-barbituric acids, and then decreasing rapidly to small figures for ethyl and allyl octyls. The only outstanding exception is diallylbarbituric acid, although in general the unsaturated members are somewhat more effective than the coefficients would lead us to expect.

Within the last year, Barlow and associates[4] have carefully compared a number of barbiturates with particular reference to efficiency in preanesthetic sedation. They place Nembutal (Pentobarbital) at the top,

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(4) Barlow, Duncan and Gledhill, J. *Pharmacol.*, 41, 366 (1931)

followed by Pernocton and Dial; barbital and phenobarbital were found relatively ineffective. If we employ, instead of the pharmacologic data recently published comparisons of certain members when used intravenously in human beings, the correlation is even closer; for instance, both Fitch, Waters and Tatum[5] and Lundy[6] have reported Nembutal twice as effective as Amytal and "somewhat" more effective than Pernocton, and we find the coefficients of 4.4, 2.8 and 4.3, respectively.

Since the theory of Meyer and Overton is based essentially upon the high lipoid content of nerve tissue, it seemed of interest to determine the distribution of various barbiturates between water and a chemically neutral medium such as ash-free charcoal.[7] Adsorption (by 1 g. of charcoal) from (300 cc. of a 0.12%) aqueous solution was remarkably rapid, equilibrium with resultant removal of 75% or better of the barbiturate being complete in less than fifteen minutes. To our surprise the order of the members studied follows qualitatively at least the order of hypnotic efficiency.

TABLE II

Barbiturate	% Adsorp
Dimethyl	79
Diethyl (Barbital)	88
Diallyl (Dial)	92.5
n-Butyl ethyl (Neonal)	96
i-Amyl ethyl (Amytal)	95 app.
Ethyl (1-methyl butyl) (Nembutal)	96
Octyl ethyl	83.5

Traube has suggested[8] that the surface tension of the hypnotic solution may be the deciding factor in determining its efficiency. We have, therefore, determined the surface tension of the aqueous solutions of the above barbiturates at two concentrations. Measurements were made by the De Nouy tensiometer at 20°, and the results expressed as the percentage of the normal value for water determined at the same time. From Table III, it is seen that while surface activity does increase with increasing hypnotic efficiency, it does not decrease in the octyl homologs as the theory would lead us to expect. Furthermore, Amytal is more surface active than Nembutal (Pentobarbital acid) but much less effective.

Chemical stability and rate of excretion are becoming important factors now that we appreciate the superiority of short-acting barbiturates as preanesthetic sedatives. Barbital is largely (70–80%) excreted unchanged in the urine, while with certain higher homologs the majority is apparently decomposed in the body.[9] Shonle and Keltch[10] have stated that neither Amytal nor Nembutal is eliminated as such in the urine.

(5) Fitch, Waters and Tatum, Am. J. *Surgery*, 9, 110 (1930)

(6) Lundy. *Anesthesia and Analgesia*, 9, 210 (1930).

(7) Kindly supplied by Dr. E. J. Miller

(8) Traube, *Arch. ges Physiol.*, 153, 276 (1913); 160, 51 (1915); 161, 530 (1915)

(9) Herwick, *J. Pharmacol.*, 39, 267 (1930).

(10) Shonle and Keltch, Indianapolis Meeting, A. C. S , April, 1930

TABLE III

No.	Barbiturate	Mol wt	% S. T (satd)	% S. T. 1:2000	Efficiency rating
1	Dimethyl	156	98.5	100.0	0
2	Diethyl (Barbital)	184	90.0	99.1	f
3	Ethyl *i*-propyl (Ipral)	198	94.5	98.5	f
4	i-Propyl allyl	212	84.0	97.5	++f
5	Diallyl (Dial)	208	87.5	97.5	++
6	n-Butyl ethyl (Neonal)	212	75.5	89.5	+++
7	*Sec.* butyl ethyl	212	84.0	96.0	+++
8	*Sec* -butyl allyl	224			++++
9	*n*-Amyl ethyl	226	75.0	76.5	+++
10	*i*-Amyl ethyl (Amytal)	226	77.5	76.5	+++
11	Ethyl (1-methylbutyl) (Nembutal)	226	75.0	85.5	++++
12	*Sec.*-butyl β-bromoallyl (Pernocton)	304	87.0	91.5	++++
13	Phenyl ethyl (Phenobarbital)	234	95.0	97.5	++
14	Allyl (rnethylhexylcarbinyl)	280	67.2	79.0	0
15	Ethyl (methylhexylcarbinyl)	267	75.5	..	0

A definite amount of the pure sodium salt was dissolved in carbon dioxide free water in a sealed tube and held at 100° for sixteen hours. After cooling, the contents were acidified with sulfuric acid and the liberated carbon dioxide absorbed in "Ascarite." From this, the amount of decomposition was calculated. We find that stability toward hydrolysis of the sodium salts in aqueous solution to the corresponding acetyl ureas does not run inversely parallel to hypnotic efficiency but is dependent upon the groups attached to the "5" carbon atom. The presence there of any "secondary" linkage increases stability threefold. The additional presence of the unsaturated negative β-bromoallyl group still further enhances resistance to hydrolysis of the ester linkage. In other words, we find the unexpected fact that other things being equal the powerful barbiturates containing a secondary group are on the one hand very stable in the test tube, and very unstable in the body.

TABLE IV

	Barbiturate	% Hydrolysis
1	Diethyl (Barbital)	80
2	*n*-Butyl ethyl (Neonal)	85
3	*i*-Amyl ethyl (Amytal)	79
4	Cyclohexenyl ethyl (Phanodorn)	41
5	Phenyl ethyl (Phenobarbital)	96
6	*Sec.*-butyl ethyl	28
7	Ethyl (1-methylbutyl) (Nembutal)	24
8	Ethyl *sec.*-octyl	25
9	*Sec.*-butyl β-bromoallyl (Pernocton)	165

Bancroft and Richter[11] have recently revived Bernard's theory of narcosis and presented evidence that hypnosis is in most instances associated with reversible coagulation of cell colloids. While there has been no

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(11) Bancroft and Richter, J. Phys *Chem.*, **35**, 215 (1931).

opportunity for us to study in this way the action of the barbiturates upon living cells, it does not seem to us that their findings conflict with the evidence here presented. Coagulation may be the mode of action within the cell, but there remains in clinical practice the all-important necessity for transporting the hypnotic from the point of administration to the interior of the cell through a series of transferences. Here, surface tension, absorption and more particularly lipoid solubility appear to be the limiting factors in the chain of events.

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Adsorption Experiments with Vitamins $B(B_1)$ and $G(B_2)$

BY H. C. SHERMAN AND NELLIE HALLIDAY

Seidell's adsorption of the antineuritic vitamin upon Lloyd's reagent[1] has led to considerable experimentation with this and other forms of hydrous aluminum silicate looking to partial separation of vitamins $B(B_1)$ and $G(B_2)$.[2]

The experiments here recorded were planned in quantitatively graded series, and were carried out upon protein-free milk as being a material of special scientific interest in this connection because of the extent to which it has been used as a source of the vitamin-B complex in numerous researches, beginning with the work of Osborne and Mendel.[3] As adsorbent, we have used a preparation of Lloyd's reagent kindly furnished us by Professor John Uri Lloyd. This has been used in the proportions of 5, 10, 20 and 40 g. per liter of protein-free milk, prepared as described below and adjusted to p_H 3.0 and also to p_H 4.0.

The original untreated protein-free milk, the activated Lloyd's reagent and the filtrates remaining after adsorption were tested quantitatively for their vitamin $B(B_1)$ and G potencies according to methods previously developed in this Laboratory.* The preparations were fed in graded amounts corresponding to definite quantities of protein-free milk or of the original skimmed milk powder. No attempt was made to study the possible supplementary relation of the two fractions, activated solids and remaining filtrates to each other. In view of the recent evidence suggesting

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(1) Seidell, *U. S. Pub. Health Repts.*, **31**, 364 (1916); THIS JOURNAL, **44**, 2042 (1922); *J. Biol Chem.*, **67**, 513 (1926).

(2) Jansen and Donath, *Proc. k. akad. welensch. Amsterdam*, **29**, 1390 (1926); Salmon, Guerrant and Hays, *J. Biol. Chem.*, **76**, 487 (1928); *ibid.*, **80**, 91 (1928); Williams and Waterman, *ibid.*, **78**, 311 (1928); Hunt, *ibid.*, **79**, 723 (1928); Guha and Drummond, *Biochem. J.*, **23**, 880 (1929); Evans and Lepkovsky. *J. Nutrition*, **3**, 353 (1930).

(3) Osborne and Mendel, Carnegie Inst. Washington, Pub. No. 156 (1911).

(4) Chase and Sherman, THIS JOURNAL, **63**, 3506 (1931); Bourquin and Sherman, *ibid.*, **63**, 3501 (1931).

the multiple nature of both the more heat labile and the more heat stable components of the vitamin-B complex and in view of the further investigations of Halliday and of Stiebeling: it is conceivable that some part of our apparent losses in vitamin potencies might possibly be due to a partial separation of the component factors of what are here treated as entities, i. *e.*, vitamins B and G, respectively.

This would not change the general bearings of our findings, but might influence slightly the details of the numerical data or of graphs plotted therefrom. For this reason and in the interest of brevity, the details are omitted from this paper. They may be consulted, if desired, in the privately printed dissertation of the junior author, copies of which have been distributed by Columbia University to a number of other university libraries.

Experimental Procedure

The protein-free milk was prepared as follows. A weighed quantity of skimmed milk powder was thoroughly mixed with eight times its weight of distilled water. To this mixture was added sufficient 0.3 M hydrochloric acid (usually 175 cc. per 100 g. of the milk powder) to completely precipitate the casein. After filtration through several layers of cheesecloth, the resulting filtrate was heated to boiling for five minutes to precipitate the heat coagulable protein and filtered through filter paper. The filtrate or protein-free milk had a reaction as determined by electrometric measurements using a hydrogen electrode and saturated calomel half-cell, of about P_H 4.2.

The protein-free milk volume was measured and divided into three aliquots; one aliquot after being adjusted to about P_H 5.7 with 0.2 M sodium hydroxide was without further treatment fed as vitamin B(B_1) and as vitamin G supplements; a second aliquot after being adjusted to P_H 3.0 with 0.3 M hydrochloric acid was further divided and each portion treated with a definite amount of Lloyd's reagent; the third aliquot was adjusted to P_H 4.0 previous to treatment with the different amounts of Lloyd's reagent. The Lloyd's reagent was added to portions of the protein-free milk adjusted to P_H 3.0 and (or) P_H 4.0 in ratios of 40, 20, 10 and 5 g., respectively, per liter of the protein-free milk. The adsorbent and solutions, after thorough mixing, were allowed to stand in contact in a refrigerator overnight. The "activated solids" were then separated by use of a Büchner funnel, washed with dilute hydrochloric acid (P_H 3.0 or P_H 4.0), dried at room temperature for twenty-four hours, pulverized and used thus as vitamin B(B_1) and as vitamin G supplements for the experimental animals. Each filtrate remaining after adsorption was evaporated under reduced pressure (30–40°) to approximately one-fourth of its original volume, adjusted to about P_H 5.7 and the respective volumes measured in order that known equivalents in terms of the protein-free milk could be fed for measurements of their vitamin B(B_1) and vitamin G potencies.

These several preparations were kept in an ice-box and freshly prepared each week. As supplements the liquid preparations were fed in six equal amounts weekly, the solid preparations were incorporated in the basal rations each week using such quantities of the basal ration for this as would be somewhat less than the animal would eat during the week as judged by previous weekly food records, basal diet alone being fed for the remainder of the week. The experimental animals were in all cases weighed weekly.

Results

Animals receiving the original skimmed milk powder and animals receiving corresponding amounts of untreated protein-free milk as sources

(5) Halliday, *J. Biol. Chem.*, 96, 479 (1932); Stiebeling, *Proc. Soc. Exptl. Biol. Med.*, 29, 1156 (1932).

of vitamin $B(B_1)$ showed practically the same average responses in growth, indicating little or no loss of potency in the preparation of the protein-free milk. The same was true as regards the vitamin G content of the protein-free milk.

When the amount of Lloyd's reagent employed was 40, 20, 10 or 5 g. per liter of protein-free milk, the filtrates were without appreciable vitamin $B(B_1)$ activity; approximately 50% of the original vitamin $B(B_1)$ potency was usually accounted for in the activated solids. Whether the protein-free milk had been adjusted to P_H 3.0 or to P_H 4.0 previous to the addition of the adsorbent made no significant difference in the vitamin **B** or in the vitamin G potencies of the activated solids or filtrates. In all cases the difference between the average growth rates of animals receiving, respectively, the product prepared from protein-free milk adjusted to P_H 3.0 and that adjusted to P_H 4.0 was less than the probable error of that difference. The addition of the adsorbent caused a decrease in the acidity of the solutions, and this was more marked with the larger amounts of adsorbent. When the adsorption processes were carried out in an atmosphere of nitrogen rather than air, the activated solids instead of showing only 50% of the original vitamin $B(B_1)$ of the protein-free milk showed from 60 to 70% of the potency. The activated solids carried about one-third of the vitamin **G** potency of the protein-free milk and the filtrates regularly contained about one-sixth of this original potency, so that in all 50% of the vitamin G activity of the protein-free milk could be accounted for after the fractionation by adsorption with Lloyd's reagent.

When the adsorption processes were carried out in an atmosphere of nitrogen both activated solids and filtrates showed somewhat higher vitamin G potency than when the adsorption was carried out in air, the recovery under nitrogen being about two-thirds as compared with about one-half in the presence of air. The nature of these apparent losses is being studied further.

Summary

1. Protein-free milk may be prepared from skimmed milk powder without appreciable loss of vitamin $B(B_1)$ or vitamin $G(B_2)$ potency.

2. Vitamin $B(B_1)$ is relatively more efficiently adsorbed from protein-free milk on Lloyd's reagent than is vitamin G.

3. Varying the amount of Lloyd's reagent used from 5 to 40 g. per liter of protein-free milk (initially adjusted to P_H 3.0 or P_H 4.0) did not result in appreciable differences in the amounts of vitamin $B(B_1)$ or vitamin $G(B_2)$ adsorbed.

4. Under the conditions of these experiments approximately one-half of the vitamin $B(B_1)$ potency and one-third of the vitamin **G** potency of the original protein-free milk was adsorbed on the Lloyd's reagent; but no appreciable amount of the original vitamin $B(B_1)$ potency and only about

one-sixth of the vitamin G potency was shown by the filtrates after removal of the activated solids.

5. When the adsorption processes were carried out in an atmosphere of nitrogen rather than air and under otherwise comparable conditions, the activated solids were somewhat more potent in both vitamins B(B_1) and G and the filtrates were more potent in vitamin G. The apparent losses are being studied in other ways and in the light of the newer evidence as to probable multiple nature of vitamins B and G.

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Liquid Ketene and Ketene Polymers

BY CHARLES D. HURD, AMOS D. SWEET AND CHARLES L. THOMAS

In a study of liquid ketene which was prepared by liquefaction from the gas stream from the pyrolysis of acetone, a few new items of interest were found. (1). Polymerization, which occurs even at $-80°$, may be retarded by a trace of hydroquinone (2 mg. for 2 cc. of liquid). (2). No reaction was observed in twelve hours between liquid ketene and metallic sodium or sodium–potassium (1:2) alloy or sodamide (suspended in toluene) or isoprene. Thus, the alkali metals did not bring about rearrangement of ketene into hydroxyacetylene ($HC{\equiv}COH$) and the isoprene did not add in the way it adds to maleic anhydride.[1] Possibly the low temperature was a contributing factor in these negative effects. **(3).** An extremely vigorous reaction was observed between liquid ketene and the Grignard reagent. Even at $-78°$ and diluted with ether the reaction with n-butyl- or phenylmagnesium bromide was so vigorous that each added drop of Grignard reagent produced a crackling sound. The voluminous yellow solid which precipitated hydrolyzed to a sticky gum from which nothing was obtained. This is a modification of the experiment of Deakin and Wilsmore.[2] They diluted gaseous ketene with hydrogen and observed a very complex reaction as it was passed into a cold ether solution of methylmagnesium bromide.

(4). Tertiary alcohols react with liquid ketene giving tert-alkyl acetates. In previous unpublished work,[3] it was demonstrated that ketene gas also acetylates these tertiary alcohols but less effectively. This confirms Davis and Murray[4] who stated: "Tertiary butyl acetate, a typical tertiary ester, is suitably prepared by the action of ketene with tertiary butanol." However, Davis and Murray cited no experimental work.

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(1) Diels and Alder, *Ann.*, 460, 98 (1928); 470, 62 (1929); 478, 137 (1930).
(2) Deakin and Wilsmore, *J. Chem. Soc.*, 97, 1968 (1910).
(3) Hurd and Martin, M.S. thesis of K. E. Martin, Northwestern University, 1928
(4) Davis and Murray, *Ind. Eng. Chem.*, **18**, 846 (1926).

Six cc. of *tert.*-butyl alcohol (b. p. 79.5–80°) at 20° was added dropwise during ten minutes to 6 cc. of liquid ketene at −78°. The alcohol solidified but gradually dissolved. After three hours the mixture was distilled. About 3 cc. of the alcohol was recovered and 4.5 cc. of a *tert.*-butyl acetate fraction (92–98") formed which, on redistillation, gave these constants: b. p. 96°; $n_{D}^{18.5}$ 1.386 as compared with the recorded value[6] of 1.3887.

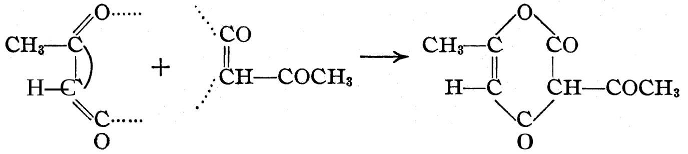
Similarly, 5 cc. each of *tert.*-pentyl alcohol and ketene were admixed and the mixture distilled after three hours. Three cc. was collected below 120° and 2.6 cc. above 130". The *tert.*-pentyl acetate fraction, b. p. 120–130°, was 4.0 cc. On redistillation, it boiled at 123° (747 mm.); n_{D}^{20} 1.392.

Polymers of Ketene.—It was found that both ketene dimer and dehydroacetic acid were by-products in the preparation of ketene from acetone. Accordingly, an apparatus was constructed to facilitate the separation of these polymers. Acetone was boiled into the bottom of a vertical Pyrex reaction tube (2.5 X 90 cm.) the temperature of which was held at 700° by an electric furnace. The escaping gases were directed downward through a water cooled condenser and the condensate returned to the acetone flask to be recycled. The acetone which remained in the gas stream was separated with a coil condenser at −15". When acetone was boiled into the apparatus at such a rate that 2 drops per second of condensed acetone fell from the water condenser, then the flow of ketene in the uncondensed gas was 0.3 mole per hour. Part of this ketene could be liquefied in a trap at −78° but for complete removal a liquid air trap was necessary.

Fractionation of the condensate to 70° at the end of a day's run left a residue weighing 30–50 g. From 15 liters of acetone, 300 g. of this residue was obtained. Two hundred grams of this was crude ketene dimer, b. p. 120–130°, and 100 g. was still higher boiling. Both fractions were contaminated with some acetic anhydride, the presence of which was no doubt due to the fact that the technical acetone used contains some water: $2CH_2CO + H_2O \longrightarrow (CH_3CO)_2O$. The identity of ketene dimer was confirmed not only by its boiling point, 125°, but also by its derivative with aniline, namely, acetoacetanilide, m. p. 84".

The 100 g. of higher boiling residue was about two-fifths dehydroacetic acid. This was separated by two methods: (1) chilling in a refrigerator and recrystallization of the crystals thus produced from either water or benzene; (2) vacuum distillation. The melting point by either method was 108" and it was not depressed by mixing with known dehydroacetic acid. In the vacuum distillation of a 25-g. portion of the 100 g. of residue, 3 cc. of liquid distillate was collected, after which a 10-g fraction appeared which solidified on cooling. This was dehydroacetic acid. The higher boiling residue was a brown tar which appeared to decompose as it was distilled further.

Chick and Wilsmore[6] obtained dehydroacetic acid[7] by treating ketene dimer with a little pyridine. This polymerization is most simply explained on the assumption that ketene dimer is acetylketene rather than cyclobutanedione. Using partial valence formulas it is a straightforward addition



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(5) Smith and Olsson, Z. *physik. Chem.*, **118**, 99 (1925).

(6) Chick and Wilsmore, *J. Chem Soc* , **93**, 946 (1908): **97**, 1987 (1910).

(7) For its structure, see Rassweiler and Adams, THIS JOURNAL, **46**, 2758 (1924).

The acetylketene formula may be reconciled with Chick and Wilsmore's observation that ketene dimer gives rise to γ-bromoacetoacetyl bromide on bromination by assuming the following rearrangement

$$CH_3COCHBrCOBr \longrightarrow CH_2BrCOCH_2COBr$$

That the —COBr group may facilitate this rearrangement is very reasonable in view of the similar rearrangement[8] which is promoted by the —$COOC_2H_5$ group: $CH_3COCHBrCOOC_2H_5 \longrightarrow CH_2BrCOCH_2COOC_2H_5$.

In a recent paper by Berl and Kullman[9] entitled "Preparation of Ketene by the Catalytic Decomposition of Acetone," acetone vapors were decomposed in an apparatus of the customary type.[10] One gains the impression that a pronounced catalysis was observed, but as a matter of fact any catalytic effects were very small. The yield of ketene depended in large measure on the temperature (about 700°, whereas for useful catalysis one might anticipate about 300 or 400°) and on the ratio of vaporized to decomposed acetone. The best yield (77%) was obtained at 680° with the above ratio as 22:1. The fact that a V_2O_5 filler was present in the reaction tube seems less important than Berl and Kullmann infer, for similar results were obtained[11] with about the same conditions when the reaction tube was quite empty.

Summary

Liquid ketene fails to react with sodium, sodium-potassium, sodamide or isoprene. Its reaction with Grignard reagents is violent and complex. Liquid ketene reacts satisfactorily with tert-butyl and tert-pentyl alcohols to give the tert-alkyl acetates.

Ketene dimer and dehydroacetic acid are by-products of the ketene synthesis. A method of isolating them is described.

EVANSTON, ILLINOIS

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(8) Hantzsch, Ber., 27, 355, 3168 (1894).

(9) Berl and Kullmann, ibid.. 65, 1114 (1932).

(10) "Organic Syntheses," John Wiley and Sons, New York, 1932, Collective Vol. I, p. 326.

(11) Hurd and Dull, THIS JOURNAL, 54, 3428 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNITED STATES GEOLOGICAL SURVEY, DEPARTMENT OF THE INTERIOR]

The Analysis and Composition of Fatty Material Produced by the Decomposition of Herring in Sea Water[1]

BY ROGER C. WELLS AND E. THEODORE ERICKSON

The widely accepted theory of the origin of petroleum in sedimentary deposits through the decomposition of organic matter derived from plants or animals, or both, adds special interest and importance to our knowledge of observable changes in such materials under natural conditions. The material described in this paper, found to be calcium and magnesium salts of fatty acids, came from a wrecked boat load of herring, and had apparently resulted from the action of sea water on the herring, though for exactly how long a period is not known.

This material was collected at Mole Harbor, Admiralty Island, Alaska, by Mr. A. Hasselborg, and sent to Dr. David White, of the United States Geological Survey, who turned it over to the Chemical Laboratory of the Survey for study and analysis. It was reported that the wreck had long rested in fifteen fathoms of water. As it finally broke up Mr. Hasselborg observed that pieces of this particular material rose to the surface, broke up, and gradually sank again. The material, as received in Washington, sank in sea water of specific gravity 1.03, unlike free fatty acids, which float. This fact indicates that such material might be deposited directly in sediments. The sample consisted of fairly uniform pieces with a greasy feel, somewhat porous and nearly white in appearance, with some finer broken material. The larger pieces seemed to consist of layers.

ANALYSIS (BY E. T. ERICKSON) OF FATTY MATERIAL DERIVED FROM THE DECOMPOSITION OF HERRING

C	**63.63**
H	**10.06**
N	**0.43**
S	**0.93**
Ca	**5.00**
Mg	**0.82**
K	**0.03**
Na	**0.26**
Fe_2O_3	Trace
Al_2O_3	**0.12**
PO_4	**0.19**
SO_4, CO_3	None
NaCl	**2.72**
SiO_2	**0.20**
	84.39
Undetermined, mainly oxygen, by difference	**15.61**
	100.00

This analysis was made with material dried at 105° for one hour, during which the loss was 5.90%. This loss was found to be practically all the water and did not include a significant quantity of organic matter. Nitrogen was determined by the Dumas method, and sulfur by the Carius method. The difference represents mainly organic oxygen. The most striking features shown by the analysis are the high percentages of calcium and magnesium and low percentage of phosphate;

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[1] Published by permission of the Director of the U. S. Geological Survey.

the calcium cannot be present as calcium phosphate or carbonate but must be mainly in an organic compound.

Further tests to determine the identity of the organic material were made by decomposing it with hydrochloric acid. The resulting insoluble fatty acids were filtered off, dried, extracted with benzene, and the unsaturated and saturated acids separated by the Varrentrap method.[2] The saturated fatty acids probably include palmitic acid, myristic acid, and some acids of lower molecular weight. These conclusions are based on determinations of the melting points of the fractionated material. Three small fractions were separated by adding magnesium acetate to the alcoholic solution of the mixed acids. These fractions, freed from magnesium, had melting and solidifying points of 58 and 56°, 5S.5 and 55°, and 57 and 55.5°, respectively. The melting and solidifying points of the original saturated fatty acid material were 53 and 51°; those of material remaining from the fractionation 48 and 47".

Stearic acid did not seem to be present, although Lexow[3] states that its glyceryl ester occurs in Norwegian herring oil, together with the esters of palmitic and myristic acids. On the other hand, Fryer and Weston[4] state that the "stearine" obtained from Japanese herring and other fishes is chiefly "palmitin." Tsujimoto[5] isolated palmitic and myristic acids from fatty material obtained from the great herring at Hokkaido (Hokushu) but found the glyceryl ester of stearic acid present in relatively small quantities. Thus the range of saturated fatty acids recovered from the Mole Harbor material is about the same as that in glyceryl ester form in herring oil.

The unsaturated fatty acid portion was amber colored, of an oil-like appearance, and gave an iodine adsorption figure of 70 by the Wijs method. This figure is low compared with that of known herring oils. Lexow,[6] in 120 Norwegian herring oils collected from different localities and at different seasons of the year, found a high average of 148 during August and a low average of 115 during March.

A summary of the findings in the quantitative work is given in the following table.

The non-saponifiable matter yielded a small quantity of the characteristic cholesterol precipitate with digitonin. This precipitate was converted to acetate, the melting point of which confirmed the presence of cholesterol. Because of lack of material the state of occurrence of the cholesterol was not determined.

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[2] Holde. "The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes," Trans. by E. Mueller, John Wiley and Sons, Inc., New York, 1922, p. 371.

[3] Lexow, *Chem. Umschau Fette, Öle, Wachse, Harze, 28,* Part 7, 85 (1921).

[4] Fryer and Weston, "Technical Handbook of Oils, Fats and Waxes," Cambridge Press, 1917, Vol. I, p. 101.

[5] Tsujimoto, *J. Soc. Chem. Ind. Japan, 29,* 195–202; *Chem. Abs.,* 20, 2912 (1926).

[6] Lexow, *Chem. Umschau Fette, Öle, Wachse, Harze, 29, Part* 9, 110–113 (1922).

SUMMARY OF CHEMICAL SEPARATIONS ON SAMPLE FROM MOLE HARBOR

		Per cent.
Loss on heating for one hour at 105°		5.90
Organic matter extracted with benzene after treatment of the sample with hydrochloric acid	Unsaturated fatty acids	8.20
	Saturated fatty acids	64.50
	Non-saponifiable matter	0.60
Protein calculated from nitrogen (N X 6.25)		2.80
Inorganic matter, including sulfur and 2.72 NaCl		10.27
Undetermined, including possibly some carbohydrate substance and oxygen required by sulfur compounds, less replaceable hydrogen of fatty acids (0.33)		7.73
		100.00

The material insoluble in benzene was found on ignition to contain some organic matter. At the beginning of the ignition carbonization was noted, followed by the characteristic odor of burning protein. The material extracted with benzene gave no evidence of undecomposed glyceryl ester. Most of the fatty acids in the original sample must have been combined with the inorganic bases, though some free acids may have been present.

Geochemical Features.—The well-known Engler–Hofer theory of the origin of petroleum from fatty materials in sediments[7] seems to assume that the fatty substances are isolated in some way from the saline constituents of the water of the sediments during the stage of microbiochemical decomposition, so that calcium and magnesium compounds of the liberated fatty acids are not formed. According to this theory the fatty substances first change into free fatty acids and glycerin, either by hydrolysis or by microbiochemical-fermentation, or both. Eventually, the fatty acids are assumed to split off carbon dioxide and the hydrocarbons to polymerize into petroleum. It is impossible here to go into the many details of this theory. The present writers wish to emphasize a possibility not heretofore considered—that calcium and magnesium salts may be formed even before or as the material is inclosed in sediments, and that such compounds deposited with the sediments can then yield petroleum under proper environmental conditions, whether by heat, base exchange or otherwise.

The experiments described below were made to find out whether the material from Mole Harbor would show any marked disinclination to form oil upon thermal decomposition in sealed glass tubes. They indicate that such material requires but a slightly higher temperature than free fatty acid material to form oil.

The free fatty acid, palmitic acid, some calcium palmitate and the herring residue from Mole Harbor were each subjected to successive heat treatments in sealed glass tubes during eighteen-hour intervals at 200, 300 and 350° and then finally for seven days at 350°, and any effects that might indicate decomposition noted.

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[7] "Das Erdöl," Leipzig, 1909, II Band, 114–128. E. Engler, *Petroleum Zeitschrift*, 7, 399403 (1912); "Das Erdol und seine Verwandten," Braunschweig, 1922, p. 329.

At 200° the palmitic acid and the herring residue darkened slightly and each of the materials melted into a mass that solidified on cooling.

At 300° the palmitic acid darkened further in color and still solidified on cooling. The calcium palmitate and the herring residue remained apparently unchanged from the previous heat treatment.

Under the initial heat treatment at 350° for eighteen hours the palmitic acid yielded a still darker brownish product that remained fluid at ordinary room temperatures. The calcium palmitate and herring residue changed but slightly in color and gave but little appearance of having undergone any further decomposition.

In the further heating for seven days at 350° all the materials yielded a greenish fluorescent petroleum-like product. The yield was similar in each experiment and appeared relatively high compared to the quantity of original material taken. When the tube which had held the calcium palmitate was opened considerable pressure was shown. The odor resembled gasolene. The residue consisted of carbonaceous matter, a little tiapthenic-like oil, and calcium carbonate.

Summary

This paper describes the analysis of calcium and magnesium salts of fatty acids derived from herring buried under sea water, and discusses some geochemical possibilities related to the origin of petroleum in sedimentary deposits.

WASHINGTON. D. C.

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[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

The Preparation and Optical Resolution of Ammonium *dl*-Alpha-Bromocamphor-Pi-Sulfonate

BY A. W. INGERSOLL AND S. H. BABCOCK

The preparation of many asymmetric acids and bases is necessary for a comprehensive study of optically isomeric salts.[1] Obviously those acids and bases whose racemic forms are capable of resolution and whose active forms are useful resolving agents are especially valuable. Also the racemic forms are as necessary for this type of study as the active forms. Bases suitable for resolution work and available in both the racemic and active forms are fairly numerous, but there are relatively few acids of this description. Thus d-tartaric, *l*-malic, d-camphor-10-sulfonic and *d*-α-bromocamphor-n-sulfonic acids are the only ones that have been much used. The optical antipodes and the racemic forms of these, though known in

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[1] (a) Ingersoll and White, THIS JOURNAL, 54,274 (1932); (b) Ingersoll and **Burns,** *ibid.*, 54, 4712 (1932).

most cases, are comparatively uncommon. Satisfactory methods for preparing the rarer varieties of these and other suitable acids are therefore being studied. The preparation of dl-a-bromocamphor-n-sulfonic acid (as ammonium salt) and a simple method for resolving it into the pure d- and l-forms are described in this paper.

d-a-Bromocamphor-n-sulfonicacid has found extensive use as a resolving agent since its advantages for this purpose were pointed out by Pope and Peachey.[2] It is prepared by the sulfonation of d-a-bromocamphor derived from ordinary *d*-camphor[3,4] and is therefore readily accessible. The corresponding I-acid has been prepared similarly from *l*-camphor.[5] Since the latter is usually not entirely pure and is difficult to obtain, the *l*-acid is somewhat rare. The dl-acid and its simple salts appear not to have been completely described. It is said to be formed in traces when d-a-bromocamphor is sulfonated,[6] but in the few other instances in which this acid[7] or its derivatives[8,9] are mentioned in the literature, these appear to have been made only by mixing the active forms.

The method of preparation described in the present paper is based upon the direct sulfonation of dl-a-bromocamphor derived from commercial dl-camphor. This apparently simple method has not previously been described, doubtless because the necessary dl-a-bromocamphor has not been available in sufficient amounts. A method for obtaining this intermediate in good yields and large amounts was therefore first developed. It was found that dl-camphor reacts with one mole of bromine to form a semi-solid mass. This appears to contain chiefly dl-a-bromocamphor and the isomeric dl-a'-bromocamphor, together with dl-camphor and *dl*-α,α'-dibromocamphor. The separation of crystalline dl-a-bromocamphor was at first troublesome because of its excessive solubility and the presence of the even more soluble by-products. However, it was found that most of the a'-compound was converted to the a-compound by heating the mixture and then crystallizing the a-compound from slightly alkaline alcohol at -10°. This method of isomerizing the a'-compound was suggested by the experience of Marsh[10] and of Lowry[11] in the preparation of d-a-bromocamphor from d-camphor, though in this case the less soluble active compound crystallized readily. Haller[12] has described the bromination product

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[2] Pope and Peachey, J. *Chem. Soc.*, 73,893 (1898).

[3] Kipping and Pope, *ibid.*, 67,356 (1895).

[4] Pope and Read, *ibid.*, 97,2199 (1910).

[5] Pope and Harvey, *ibid.*, 79, 74 (1901).

[6] Kipping, *ibid.*, 79, 370 (1901).

[7] Pope and Gibson, *ibid.*, 97,2207 (1910).

[8] Perkin and Robinson, *ibid.*, 99,788 (1911).

[9] Pope and Read, *ibid.*, 101,758 (1912).

[10] Marsh, J. *Chem. Soc.*, 59,968 (1891).

[11] Lowry, *ibid.*, 89, 1033 (1906).

[12] Haller, *Compt. rend.*, 105, 66 (1887).

of *dl*-camphor as a "buttery mass." He was unable to crystallize this under any conditions, but did prepare a specimen of *dl*-α-bromocamphor, m. p. 51°, by mixing the active forms. His description of this compound was confirmed.

dl-α-Bromocamphor was sulfonated with chlorosulfonic acid and ammonium *dl*-α-bromocamphor-π-sulfonate isolated. Although the yield was somewhat low (30–35%) it was not difficult to prepare large amounts of the pure salt. The optical resolution was then carried out. In a recent paper[1b] it was shown that the active forms of α-*p*-tolylethylamine can easily be prepared in good yields by resolving the dl-base with d-camphoric acid. When ammonium *dl*-α-bromocamphor-π-sulfonate is combined with the *l*-form of this base in dilute acetic acid, the *l*B*l*A salt and, in smaller amounts, the *l*B*d*A salt can be gotten pure from the solution. The ammonium salts of the corresponding acids were obtained from these salts in good yields. This method of resolution appears to be more satisfactory than that of Pope and Gibson.[7] These workers resolved the dl-acid, whose source was not mentioned, by means of *d*-1,2-dihydropapaverine (*d*-pavine). This base had been obtained from synthetic dl-pavine by resolution with d-a-bromocamphor-a-sulfonic acid. Although the resolution was apparently not difficult, the base employed is too rare for general use.

Experimental

Preparation **of *dl*-α-Bromocamphor.**—*dl*-Camphor (152 g.) was placed in a three-necked flask on a steam-bath and bromine (163 g.) was slowly added while the mixture was stirred.[13] It gradually liquefied and hydrogen bromide was evolved. Including two hours for adding the bromine, the mixture was heated for ten hours. While still warm it was then poured with stirring into two liters of water containing a few grams of sodium sulfite. The waxy solid, when broken up, filtered, washed with fresh water and air-dried, weighed 220–235 g. and was slightly brown. Many unsuccessful attempts were made to crystallize the substance from the usual organic solvents, in which it is very soluble. Finally it was found that a filtered solution in 95% ethanol (1 cc. per gram), when held at −10° in the freezing chamber of an electric refrigerator and inoculated with crude or previously purified material, slowly deposited about half the material as a colorless, crystalline mass, m. p. 47–49°. Recrystallization under similar conditions gave back about 80% of the first crop, m. p. 49–50°. On concentration the mother liquors gave some crystalline material, but principally a reddish-brown oil. The initial yield of crystalline product was considerably increased when the alcoholic solution of the crude product or the oil was made slightly alkaline with sodium hydroxide and warmed for a few minutes before cooling. Also the oily material from several runs, when distilled at 4 mm., was separated into a small forerun (chiefly dl-camphor), a dark residue, and a main fraction boiling at 108°. This solidified, and then melted at 44–46°. It contained 34.2% of bromine instead of 34.6% calculated for monobromocamphor, and when crystallized from alkaline alcohol gave back about half its weight as crystals, m. p. 49–50'. By thus alternately distilling and crystallizing an average yield of 178 g. (77%) of crystals, melting at 49° or higher. was obtained in five runs.

Pure dl-a-bromocamphor separates from 95% ethanol in large, monoclinic hemimorphic crystals, melting at 50.5–51° (corr.), in agreement with Haller's value.

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[13] Armstrong and Mathews, *Chem. News*, **37**, 4 (1878).

Anal. Calcd. for $C_{10}H_{15}OBr$: Br, 34.6. Found: Br, 34.4.

Ammonium-dl-or-Bromocamphor-T-sulfonate—Pure dl-a-bromocamphor was sulfonated in 230-g. lots with chlorosulfonicacid and converted to a solution containing the ammonium sulfonate. The procedure used by **Kipping** and Pope[3] for the preparation of the corresponding dextro compound was followed. When the initially dark brown solution was concentrated in stages the crude ammonium salt separated and was systematically recrystallized. Much of the material remained as a sirupy residue and the yield of pure salt (100–115 g. or 30–35%) is considerably lower than claimed for the dextro salt.

The pure salt crystallizes from water as a dense crystalline mass or in thick transparent prisms and is anhydrous. It melts with decomposition at 250–254'. The solubility is 15.9 g. per 100 g. of water at 25°. This is smaller than that of the corresponding d-salt, which was found to be 20.6 g. at 25°. The crystal form is also different.

Anal. Calcd. for $C_{10}H_{18}O_4NSBr$: N, 4.27; Br, 24.36. Found: N, 4.25; Br. 24.69.

Resolution of Ammonium dl-a-Bromocamphor-T-sulfonate.—The ammonium salt (49.2 g.) was dissolved in 400 cc. of boiling water and 20.3 g. of **l-α-p-tolylethylamine** and 13 g. of glacial acetic acid were added. Upon cooling most of the salt separated as a colorless oil and then solidified. This was redissolved and the solution inoculated with a sample of the solid. The first fraction of crystals then obtained on cooling was levorotatory, but successive fractions were alternately dextro- and levorotatory. After some experimentation it was found that the less soluble *l*B*l*A salt tends to form large prisms on the bottom of the vessel while the *l*B*d*A salt forms needles filling the solution Also the salts differ more in solubility at 50–80° than at lower temperatures. Hence when levorotatory fractions were recrystallized at 80 to 50° from about seven parts of water, after inoculation with the prisms, principally the *l*B*l*A salt separated. The warm mother liquor, when decanted and cooled, then gave strongly dextrorotatory deposits. By judicious combination of fractions similar in appearance and rotation and inoculation with the appropriate crystals, there was soon obtained about 75% of the *l*B*l*A salt and 55% of the *l*B*d*A. The intermediate fractions could be further separated but it was better to combine them with similar fractions from following runs The total yields of the salts in three runs were then 92 g. (89%) and 80 g. (76%), respectively.

l-α-p-Tolylethylamine-l-α-bromocamphor-π-sulfonate forms coarse, hydrated prisms, solubility 2.10 g. per 100 g. of water at 25°. The anhydrous salt melts at 165" (corr.).

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$: H_2O, 3.87. Found: H_2O, 3.97.

Rotation. Hydrated salt, 0.8445 g. made up to 50 cc. in water gave α_D^{25} −2.12 in 2 dm.; $[\alpha]_D^{25}$ −62.7'; M_D −291" (10^2).

l-α-p-Tolylethylamine-d-α-bromocamphor-π-sulfonate crystallizes initially in needles or narrow prisms. These change to irregular masses on standing in the solution for several days; both forms are the monohydrate. The needles lose their water on exposure to air for several days, and then melt at 232' (corr.). The solubility (hydrated needles) is 2.96 g. per 100 g. of water at 25°.

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$: H_2O, 3.87. Found: H_2O, 3.80.

Rotatzon. Subs., 1.2297 g. (anhydrous) made up to 50 cc. in water gave α_D^{25} +3.09° in 2 dm.; $[\alpha]_D^{25}$ +59.4°; M_D +265° (10^2).

Ammonium **l-α-Bromocamphor-π-sulfonate.**—The *l*B*l*A salt described above was treated with a slight excess of dilute barium hydroxide and the base distilled with steam. The barium was completely removed with ammonium carbonate and the filtered solution evaporated to obtain the 1-ammonium salt. This resembled the familiar d-salt, and its rotation, $[\alpha]_D^{25}$ −86.6°, agrees with the value of Pope and **Harvey**.[5] The yields of recovered base and ammonium salt were nearly quantitative.

Ammonium d–a–Bromocamphor–r–sulfonate was similarly obtained from the *l*B*d*A salt. The specific rotation was +85.8°.

Summary

1. A satisfactory method for preparing dl-a-bromocamphor from *dl*-camphor is described.
2. Ammonium *dl*-*α*-bromocamphor-*π*-sulfonate was prepared from *dl-or*-bromocamphor, and this salt and its optical resolution by means of *I-a*-*p*-tolylethylamine are described.

NASHVILLE, TENNESSEE
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Higher Alkyl Sulfonates

BY VLADIMIR C. SEKERA AND C. S. MARVEL

Although alkyl esters of the aromatic sulfonic acids have long been known as alkylating agents, the real development of these reagents has been more recent and even now they are used only for the unusual alkylation reactions. The alkyl halides and sulfates are the common reagents for introducing alkyl groups and are unquestionably the most useful reagents for the lower molecular weight radicals. However, the higher alkyl halides (ten carbons or more) are somewhat sluggish in their alkylation reactions and the higher sulfates are not easily obtained. The work which is reported in this paper was undertaken in order to find a satisfactory method of preparing the higher aliphatic esters of the aromatic sulfonic acids, to study these esters as alkylating agents, and to compare the corresponding esters of aliphatic sulfonic acids and aromatic sulfonic acids in simple alkylation reactions.

It has been found that the method of preparing sulfonic acid esters from an alcohol, a sulfonyl chloride and pyridine can be extended to the alkyl esters of both aliphatic and aromatic sulfonic acids. Patterson and Frew[1] were apparently the first to use this general method. Ferns and Lapworth[2] pointed out the difficulty of obtaining ethyl and benzyl esters of sulfonic acids because they readily combined with pyridine to give water-soluble products which were evidently quaternary ammonium salts. However, this side reaction has not been found to be serious with the higher alkyl esters when they were prepared at 0°. The yields of esters which were obtained varied from 60–80% of the theoretical amounts.

Two series of esters, the *p*-toluenesulfonates and the *p*-bromobenzenesulfonates, were prepared from the higher normal alcohols with an even

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[1] Patterson and Frew, *J. Chem. Soc.*, 89,332 (1906).

[2] Ferns and Lapworth. *ibid.*, 101, 273 (1912).

number of carbon atoms. These esters are solids which all melt below 65° yet are easily purified by recrystallization from petroleum ether and seem to be of promise as derivatives for identification.

A few experiments demonstrated the usefulness of the higher esters as alkylating agents. Lauryl and cetyl *p*-toluenesulfonates alkylated n-butylamine quite readily to give a mixture of the expected secondary and tertiary amines in yields which were almost identical with those obtained from n-butyl *p*-toluenesulfonate in a similar reaction. Cetyl cyanide was obtained in 85% yield from cetyl *p*-toluenesulfonate and potassium cyanide whereas the butyl ester gave only a 46% yield of cyanide. Lauryl p-toluenesulfonate combined with pyridine to give a crystalline quaternary ammonium salt in excellent yields when the two reagents were warmed together.

In order to compare the esters of aliphatic and aromatic sulfonic acids as alkylating agents, the reactions of n-butyl methanesulfonate and n-butyl p-toluenesulfonate with sodium phenolate, sodium acetate and aniline were studied. The yields of ether, ester and secondary amine, respectively, were practically the same with these two reagents. These experiments showed that the esters of the aliphatic sulfonic acids offer no advantage over the more readily available aromatic sulfonic acid esters.

Experimental

_n_-Butyl Methanesulfonate.—A mixture of 14.8 g. of n-butyl alcohol and 22.9 g. of methanesulfonyl chloride was placed in a 500-cc., three-necked flask, equipped with a mechanical stirrer and a separatory funnel and cooled in an ice–salt bath to 0°. The stirrer was started and 31.6 g. of pyridine was added slowly over a period of three to four hours. An excess of dilute hydrochloric acid was added to the cold solution to remove the pyridine and the aqueous solution was extracted with ether. The ether solution was dried over anhydrous potassium carbonate, filtered and evaporated. The ester was distilled under reduced pressure. The yield was 24.2 g. (79.5% of the theoretical amount) of a product boiling at 105–106° (6 mm.); d_4^{20} 1.1074; n_D^{20} 1.4319.

Anal. Caicd. for $C_5H_{12}O_3S$: S, 21.07. Found: S, 20.86.

_n_-Butyl _p_-Toluenesulfonate.—This ester was prepared in the same manner from 14.8 g. of *n*-butyl alcohol, 41.9 g. of *p*-toluenesulfonyl chloride and 31.6 g. of pyridine. The yield was 39.3 g. (86% of the theoretical amount) of a product boiling at 169' (4 mm.); d_4^{20} 1.1319; n_D^{20} 1.5085.

Higher **Alkyl _p_-Toluenesulfonates** and **_p_-Bromobenzenesulfonates.**—The esters of the alcohols with ten or more carbons were solids and their preparation varied slightly from the above procedure.

A solution of one equivalent of the alcohol in four equivalents of pyridine was cooled to below 20' and with stirring 1.1 equivalents of pure arylsulfonyl chloride was added in portions. The reaction mixture was stirred for about three hours after the addition was complete. The temperature of the reaction mixture was always held below 20". The reaction mixture was treated with a fairly large excess of cold dilute hydrochloric acid and the ester which separated was collected on a Biichner funnel. After drying in the air the ester was recrystallized from alcohol or better from petroleum–ether. Usually one recrystallization gave a constant melting product. The esters were prepared in 12–26 g. lots.

The esters prepared and the yields and melting points of the purified products are listed in Tables I and II.

TABLE I

SOME ALKYL ESTERS OF *p*-TOLUENESULFONIC ACID

Alkyl group	Yield, %	M. p., °C.	Analysis, % S Calcd.	Found
Lauryl	75	30	9 42	9.22
Myristyl	66	35	8.70	8.49
Cetyl	67	49	8.11	7.94
Stearyl	57	56	7.55	7.59

TABLE II

SOME ALKYL ESTERS OF *p*-BROMOBENZENESULFONIC ACID

Alkyl group	Yield, %	M. p., °C.	Analysis, % Br Calcd.	Found
Decyl	78	43–44	21.2	21.1
Lauryl	66	49	19.7	20.0
Myristyl	68	51.5	18.4	18.4
Cetyl	60	60	17.3	17.3
Stearyl	62	64–65	16.3	16.2

Alkylation Experiments. (a) **Pyridine**

n-Butyl **Pyridinium *p*-Toluenesulfonate.**—A mixture of **22.8** g. of n-butyl *p*-toluenesulfonate and **7.9** g. of pyridine was heated in an oil-bath at **130–140"** for two hours On cooling the mixture solidified and was recrystallized from a mixture of ethyl acetate and acetone. The yield of product was **27** g. (88%of the theoretical amount); m. p. 114°.

Anal. Calcd. for $C_{18}H_{21}O_3NS$: S, **10.44.** Found: S, **10.36.**

Lauryl Pyridinium *p*-Toluenesulfonate.—This quaternary ammonium salt was obtained in the same manner from **8** g. of lauryl *p*-toluenesulfonate and **1.9** g. of pyridine. The yield was **8.5** g (86% of the theoretical amount) of a product melting at 135–136° after recrystallization from acetone.

Anal. Calcd. for $C_{24}H_{37}O_3NS$: S, **7.65.** Found: S, **7.38.**

(b) n-Butylamine

***n*-Butyllaurylamine** and ***n*-Butyldilaurylamine.**—A solution of **7.3** g. of n-butylamine and **34.1** g of lauryl p-toluenesulfonate in **50** cc. of dry toluene was refluxed for about six hours. The mixture was treated with a concentrated solution of aqueous sodium hydroxide and distilled with steam to remove the toluene and any remaining hutylamine. The residue in the distilling flask was extracted with ether, and the ether solution was dried over anhydrous potassium carbonate, filtered and evaporated. The residue was distilled under reduced pressure. There was thus obtained **11.9** g. (49% of the theoretical amount) of n-butyllaurylamine, b. p. 138–140° **(6** mm.); d_4^{20} **0.8174;** n_D^{20} **1.4491;** and **6.9 g. (44%** of the theoretical amount) of *n*-butyldilaurylamine, b. p. **224–226° (6 mm.)**; d_4^{20} 0.8281; n_D^{20} **1.4582.**

Anal.[3] Calcd. for $C_{16}H_{35}N$: N, **5.81.** Found: N, **5.77** Calcd. for $C_{28}H_{59}N$: N, **3.42.** Pound: N, **3.62.**

***n*-Butylcetylamine** and ***n*-Butyldicetylamine.**—In exactly the same manner, **7.3** *g*. of *n*-butylamine and **39.4** g. of cetyl *p*-toluenesulfonate gave **15.1** g. (51% of the theoretical amount) of *n*-butylcetylamine, b. p. **193–197" (6** mm.); m. p. 31–32°; and **8.7** g.

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[3] These analyses were made by Mr. K. Eder.

(33% of the theoretical amount) of n-butyldicetylamine, b. p. 295–297° (6 mm.); m. p. 44–46°.

Anal.[3] Calcd. for $C_{20}H_{43}N$: N, 4.71. Found: N, 4.58. Calcd. for $C_{38}H_{75}N$: N, 2.69. Found: N, 2.58.

(c) Potassium Cyanide

Cetyl Cyanide.—To a solution of 13 g. of potassium cyanide in 150 cc. of water was added 39.6 g. of cetyl p-toluenesulfonate. The solution was boiled under a reflux condenser for about six hours, and then cooled and extracted with ether. The ether was evaporated and the residue was distilled under reduced pressure. The yield was 21.5 g. (86% of the theoretical amount) of cetyl cyanide which melted at 26–29°. The melting point of pure cetyl cyanide is given as 29.5–30°.[4]

n-Butyl Cyanide.—The reaction between *n*-butyl p-toluenesulfonate and potassium cyanide under similar conditions gave only 46% of the theoretical amount of n-butyl cyanide; b. p. 136–140°.

Comparison of n-Butyl Methanesulfonate with n-Butyl p-Toluenesulfonate as a Butylating Reagent. (a) Phenol.—To a solution of 9.4 g. of phenol in 40 cc. of 10% sodium hydroxide was added 22.8 g. of n-butyl p-toluenesulfonate. The mixture was gently refluxed for about three hours, cooled and extracted with ether. The ether solution was dried over potassium carbonate, filtered and evaporated On distillation of the residue under reduced pressure. a yield of 11 g. (73% of the theoretical amount) of n-butyl phenyl ether was obtained, b. p 72–73" (6 mm.); d_4^{20} 0.9515; n_D^{20} 1.5049.

When 15.2 g. of n-butyl methanesulfonate was substituted for the n-butyl p-toluenesulfonate in a similar experiment, the yield of ether was 12.2 g. (81% of the theoretical amount); b. p. 72–73' (6 mm.); d_4^{20} 0.9516; n_D^{20} 1.5046.

(b) Aniline.—A mixture of 9.3 g. of aniline and 22.8 g. of n-butyl p-toluenesulfonate was heated in an oil-bath at 130–140° for about two hours. On cooling the mixture a white solid was obtained. Addition of excess concentrated aqueous sodium hydroxide solution liberated the mixed amines. The amines were collected in ether, dried over potassium carbonate and distilled under reduced pressure. The yield of n-butylaniline was 9.6 g (64% of the theoretical amount); b. p. 115–120° (15 mm.); d_4^{20} 0.9358; n_D^{20} 1.5381.

Repetition of the experiment with the substitution of 15.2 g. of n-butyl methanesulfonate for the p-toluenesulfonate gave 10.1 g. (68% of the theoretical amount; of n-butylaniline; b p. 112–114° (9 mm.); d_4^{20} 0.9362; n_D^{20} 1.5373.

(c) Sodium Acetate.—A mixture of 13.6 g. of powdered sodium acetate ($CH_3CO_2Na\,2H_2O$) and 22.8 g. of *n*-butvl p-toluenesulfonatr was thoroughly mixed and heated to 130–140° in an oil-bath for about five hours. The mixture was then cooled, treated with 100 cc. of water and extracted with ether. On distillation 7 g. (60% of the theoretical amount) of n-butyl acetate was obtained; b. p. 123–125°; d_4^{20} 0.8797; n_D^{20} 1.3989

In a similar run 15.2 g. of *n*-butyl methanesulfonate gave 7.3 g. (63% of the theoretical amount) of *n*-butyl acetate, b. p. 123–125°; d_4^{20} 0.8799; n_D^{20} 1.3990.

Summary

1. Some higher alkyl (C_{10} and above) esters of p-toluenesulfonic acid and *p*-bromobenzenesulfonic acid have been prepared.

2. These esters have been found to be useful alkylating agents in such typical reactions as alkylation of an amine or the preparation of an alkyl

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[4] Shriner, Fulton and Burks, THIS JOURNAL, 55 (1933).

cyanide. The yields of product are approximately the same or better than can be obtained from lower alkyl sulfonates in the same reaction.

3. Comparison of n-butyl methanesulfonate with n-butyl *p*-toluenesulfonate has shown that there is no advantage of an ester of an aliphatic sulfonic acid over an ester of an aromatic sulfonic acid for alkylation reactions.

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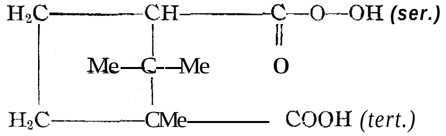
Studies in Organic Peroxides. I. Peroxides in the Camphoric Acid Series

BY NICHOLAS A. MILAS AND AMBROSE MCALEVY

Introduction

In connection with our general studies in auto-oxidation reactions[1] and especially the catalytic effects produced by organic peroxides on these and other related reactions, we had occasion to synthesize and study the properties of several new peroxides. The present communication describes the successful synthesis of some peroxides and peracids which are structurally related to camphoric acid.

A careful search of the literature revealed that up to the present time no definite peroxides of the camphoric acid series have been prepared.[2] We have obtained from camphoric anhydride and sodium peroxide a camphoric acid peracid which has the peracid group attached to the secondary carbon atom.



We have also prepared the methyl ester of this peracid by converting the tertiary monomethyl ester of camphoric acid to the acid chloride, to the ester peroxide and finally to the ester peracid.[3] The possibility of making the isomeric acid peracid through its ester derivative was precluded by the fact that the secondary monomethyl ester yields the tertiary ester secondary acid chloride[4] which gives the same ester peracid obtained from the tertiary monomethyl ester of camphoric acid. This conclusion was

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[1] Milas, THIS JOURNAL, **52**, 739 (1930); **53**, 221 (1931); *Chem. Rev.*, **10**, 295 (1932).

[2] (a) Brodie, *Proc.* Roy. *Soc.*, (London) 9, 361 (1858); **12**, 655 (1863); J. *Chem. Soc.*, **17**, 263 (1864); Ann. (Supplement), **3**, 217 (1864); (b) Kingzett, J. *Chem. Soc.*, *45*, 93 (1884); (c) Vanino and Thiele, *Ber.*, 29, 1724 (1896).

[3] Von Baeyer and Villiger, *Ber.*, *33*, 1675 (1900)

[4] Quadrat-J-Khunda, J. *Chem. Soc.*, 208 (1930); Bredt, J. prakt. *Chem.*, *133*, 87 (1932)

verified experimentally. Experiments are being conducted with the monocholesteryl and monoergosteryl esters of camphoric acid to determine the effect of the size of the alcohol group on the migration from the secondary to the tertiary carboxyl.

Experimental Part

d-Camphoric Acid Peracid.—To 200 cc. of water at 0° is added with vigorous stirring and cooling during fifteen minutes, 4.3 g. of sodium peroxide, and to this mixture is then added during one hour, 400 cc. of ethyl ether containing 10 g. of *d*-camphoric anhydride (freed from acid by shaking with saturated sodium bicarbonate solution). Stirring is continued for one hour longer, then the ether is removed and 200 cc. of fresh cold ether added. If the peracid is to be used for the estimation of unsaturation, chloroform may be substituted for ether at this stage. The mixture is then acidified in the cold with 25 cc. of 6 *N* splfuric acid, transferred to a separatory funnel and violently shaken once or twice; the ether layer is separated, shaken with about 100 cc. of saturated ammonium sulfate solution to remove any free hydrogen peroxide present, and dried overnight at 0° with anhydrous sodium sulfate. When the ether is removed at room temperature and under reduced pressure, a highly viscous liquid is obtained having a purity of 87–92% peracid; yield, 6–8 g. A white solid is obtained from the viscous liquid by treating the latter several times with ice-cold low-boiling petroleum ether (freed from unsaturated hydrocarbons) and scratching the vessel with a glass rod. The peracid is finally dried in a vacuum desiccator over concentrated sulfuric acid; m. p. 49–50° (in a sealed tube).

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.53; H, 7.46; active (O), 7.40. Found: C, 55.21; H, 7.45; active (O), 6.93, 7.16, 6.77.

Camphoric acid peracid is soluble in water, and in dilute aqueous solution hydrolyzes to yield camphoric acid and hydrogen peroxide. It is soluble in nearly all organic solvents and slightly soluble in petroleum ether. If kept at 0° and in an atmosphere of dry air, it retains its stability for several weeks. At room temperature camphoric acid peracid decomposes slowly to yield camphoric acid and oxygen, and when heated to 80–100° this reaction proceeds explosively. Its sodium salt reacts in the cold with acid chlorides and anhydrides to give acyl peroxides.

Dicamphoryl Peroxide.—To a mixture of 400 cc. of ethyl ether and 10 g. of *d*-camphoric anhydride is added slowly at 0° with vigorous stirring, a mixture of 50 g of chopped ice and 2.15 g. of sodium peroxide. After stirring for three-quarters of an hour, the ether is replaced with 400 cc. of fresh ether and the aqueous layer carefully acidified with 6 *N* sulfuric acid. The ether layer, which now contains the peroxide, is removed, dried with anhydrous sodium sulfate and the ether removed in vacuum. The solid which separates out consists of dicamphoryl peroxide and camphoric acid and to remove the latter the solid is extracted several times, each time with a few cc. of anhydrous ethyl ether, the mixture centrifuged and the Supernatant ether decanted. Finally the residue is recrystallized several times from an acetone-petroleum ether mixture (4 to 1) and the product dried in a vacuum desiccator over sulfuric acid; m. p. 142° with explosive decomposition; yield of the pure product, 3.4 g.

Anal. Calcd. for $C_{20}H_{30}O_8$: C, 60.28; H, 7.59; active (O), 4.02. Found: C, 60.34, 60.14; H, 7.83, 7.58; active (O), 4.00, 3.92.

The active oxygen was determined in acetone containing sodium iodide and acidiied with glacial acetic acid. This peroxide was also obtained in poor yields by the action of camphoric anhydride on the sodium salt of camphoric acid peracid. It is sparingly soluble in water, soluble in acetone and chloroform, somewhat soluble in ether and only slightly soluble in benzene and petroleum ether. It explodes when heated in a flame, producing substances of terpene-like odor.

Camphoryl Tert-monomethyl Ester **Sec-chloride.**—This chloride was obtained from the *tert.*-**monomethyl ester,**[5] m. p. 85.4°, and from the *sec.*-**monomethyl ester,**[5a] m. p. 77°, by the action of phosphorus trichloride in yields of **90%.**

Anal. Calcd. for $C_{11}H_{17}O_3Cl$: Cl, 15.42. Found: Cl, 15.60.

Several attempts to distil this acid chloride, even at very low pressures, resulted in its complete decomposition with the formation of camphoric anhydride, **dimethyl** ester of camphoric acid and hydrogen chloride. Upon hydrolysis it yields *tert.*-**monomethyl** ester d-camphoric acid.4

Bis-[tert.-methyl Ester **Sec.-camphoryl]** Peroxide.—To **80** g. of finely chopped ice is slowly added with shaking **5** g. of sodium peroxide, and to this mixture is added slowly in one hour with continuous shaking **150** cc of cold ethereal solution containing **10** g. of *tert.*-**methyl** ester camphoryl chloride. The mixture is violently shaken for half an hour longer to cause the complete conversion of the acid chloride to the peroxide, the ether layer separated, dried by shaking several times with fresh anhydrous sodium sulfate and the ether removed by suction in the cold. The white solid residue is then recrystallized several times from warm low-boiling petroleum ether; m. p. **102";** yield of the pure product, **3.17** g.

Anal. Calcd. for $C_{22}H_{34}O_8$: **C, 61.96; H, 7.98;** active **(O), 3.75.** Found: C, **61.52; H, 7.95;** active (O) in acetone, 3.52, 3.18.

The above preparation has been repeated using a sample of acid chloride obtained from *sec.*-**monomethyl** ester d-camphoric acid; the same peroxide has been obtained, m. p. **102°. A** mixed melting point with the peroxide obtained in the first case showed no depression.

Sec.-methyl Perester Tert.-methyl Camphoric Ester.—This **perester** is prepared by adding slowly with vigorous stirring to an ice-cold aqueous solution containing the calculated amount of the barium salt of methyl **hydroperoxide,**[6] **5** g. of *tert.*-**methyl** ester camphoryl chloride in **200** cc. of ethyl ether. The mixture is shaken at 0° for fifteen minutes longer, the ether layer separated, washed with a saturated solution of sodium bicarbonate, dried with anhydrous sodium sulfate and the ether removed in vacuum; a sirupy liquid is obtained which failed to crystallize.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, **58.99;** H, **8.26.** Found: C, **58.79;** H, **8.50.**

Analysis for active oxygen in various solvents yielded rather unsatisfactory results which are in accord with observations of other **investigators.**[6,7] The **perester** on standing at room temperature and in the presence of moisture hydrolyzes to yield methyl hydroperoxide and the original monomethyl ester of camphoric acid.

Tert.-methyl Ester **Sec.-camphoric** Peracid.—To **3** g. of **bis-[*tert.*-methyl** ester *sec.*-**camphoryl]** peroxide in **20** cc. of ethyl ether is slowly added at 0° and with vigorous stirring the calculated amount of sodium methylate, and to this mixture is then added **20** cc. of ice water, the mixture well shaken and the ether layer removed. The aqueous layer, which now contains the sodium salt of the **peracid,** is acidified in the cold with **6** N sulfuric acid and the **peracid** formed extracted with cold ethyl ether, the latter separated, dried over anhydrous sodium sulfate and removed from the **peracid** by suction at very low pressures. The residue, a highly viscous liquid **(1.5** g.), showed distinctly the properties of a **peracid,** but had a purity of only **50%.** Its purity was increased by dissolving the original liquid in pentane, cooling the solution in ice, and subsequently centrifuging

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(5) (a) Walker, J. ***Chem. Soc.,*** **61, 1088 (1892); (b) Brühl and Braunschweig, Ber., 26, 1806 (1892); (c) Haller and Blanc,** ***Compt.*** **rend., 141, 697 (1906).**

(6) Rieche and Hitz, Ber., 62, 2460 (1929).

(7) Medwedew and Alexejewa, ***ibid.,*** **65, 137 (1932).**

the suspension formed and rapidly removing it from the supernatant liquid. By repeating this process several times, a product is obtained which has an active oxygen content of 5.44%, corresponding to a purity of 78%. Other methods of purification resulted in the decomposition of the peracid.

The authors take this opportunity to express their gratitude to Prof. James F. Norris for his interest and cooperation.

Summary

1. d-Camphoric acid peracid and related peracids and peroxides have been prepared and some of their properties studied.

2. The identity of the acid chlorides obtained from the *sec.*- and *tert.*-monomethyl esters of camphoric acid has been confirmed by conversion into the same ester peroxide.

CAMBRIDGE A, MASSACHUSETTS

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Studies in Organic Peroxides. II. The Use of Camphoric Acid Peracid for the Estimation of Unsaturation

BY NICHOLAS A. MILAS AND IVAN S. CLIFF

One of the important reactions of the organic peracids is their reactivity with unsaturated groups, but more particularly with substances containing double bonds. This reaction has been studied by various investigators,[1] but cannot be generalized since it depends not only upon the reactivity of the unsaturated group which is usually governed by the adjacent groups attached to the latter,[2] but also upon the activity of the peracid itself. Furoic peracid, for example, is far more reactive than benzoperacid or camphoric acid peracid, while phthalic acid peracid fails completely to add to many unsaturated compounds.[3] Although numerous abnormalities have been reported[4] with benzoperacid and aceto-

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[1] (a) Prileschajew, *Ber.*, **42**, 4811 (1909). (b) Bergmann and co-workers, *ibid.*, **54**, 440 (1921); **56**, 2255 (1923); *Ann.*, **432**, 333 (1923). (c) Derx, *Rec. trav. chim.*, **41**, 332 (1922); (d) Hibbert and Burt, THIS JOURNAL, **47**, 2240 (1925); (e) Bauer and Kutscher, *J. prakt. Chem.*, **122**, 201 (1929); Nametkin and Brüssov, *ibid.*, **112**, 169 (1926); **115**, 56 (1927). (f) Boeseken and co-workers, *Rec. trav. chim.*, *44*, 90 (1925); **47**, 683 (1928); **49**, 95 (1930); *J. prakt. Chem.*, **131**, 285 (1931); (g) Pummerer and co-workers, *Ber.*, **62**, 1411 (1929).

[2] Meerwein and co-workers, *J. prakt. Chem.*, **113**, 9 (1926); Boeseken and Blumberger, *Rec. trav. chim.*, **45**, 838 (1926); Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1928); Smit, *Rec. trav. chim.*, **49**, *675*, 691 (1930).

[3] Milas and McAlevy, unpublished results.

[4] Arbuzov and Mikhailov, *J. prakt. Chem.*, **127**, 1, 92 (1930); Bodendorf, *Arch. Pharm.*, **268**, 491 (1930).

peracid, these peracids are the only ones used extensively for the quantitative estimation of the double bond.

The recent synthesis[5] of camphoric acid peracid suggested its use as a reagent for the estimation of unsaturation and for the preparation of oxides and glycols from the corresponding ethylenic compounds. The present communication, therefore, deals with some of the quantitative results obtained with several unsaturated compounds chosen from various branches of organic chemistry. Because of its comparative ease of preparation, camphoric acid peracid may prove a more desirable reagent than benzoperacid.

The stability of camphoric acid peracid and that of benzoperacid has been determined quantitatively in chloroform solution at 0° and at 25° and the results are plotted in Fig. 1. Both peracids were prepared at the same time and their chloroform solutions dried with anhydrous sodium sulfate to exactly the same extent, e. g., shaken twice each time with fresh anhydrous sodium sulfate, then allowed to stand over this reagent for twenty-four hours at 0°. Each solution was then filtered and divided into two portions, one kept at 0° and the other at 25°. To determine the concentration of peracid in each solution, 1-cc. portions were pipetted from time to time and titrated in the usual manner against standard sodium thiosulfate solution. The concentration of each peracid expressed in millimoles per liter of chloroform solution is plotted in Fig. 1 against time. The results seem to indicate clearly that camphoric acid peracid is slightly more stable at 0° but decidedly more stable at 25° than benzoperacid.

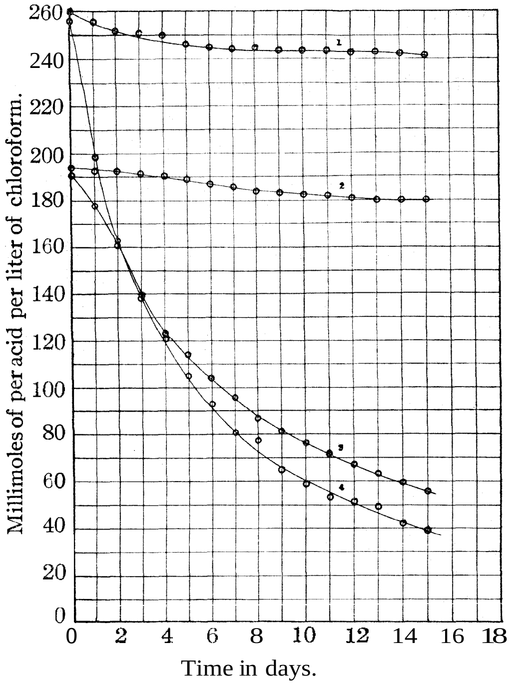

Fig. 1.—The stability of benzoperacid and camphoric acid peracid in chloroform: Curve 1, benzoperacid in chloroform at 0°; Curve 2, camphoric acid peracid in chloroform at 0°; Curve 3, camphoric acid peracid in chloroform at 25°; Curve 4, benzoperacid in chloroform at 25°.

Quantitative Estimation of **Unsaturation.**—All unsaturated substances used in this investigation were of the purest quality obtainable and in cases of doubtful purity

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[5] Milas and McAlevy, THIS JOURNAL, 55, 349 (1933).

each compound was carefully purified and its constants determined. The procedure adopted for the determination of unsaturation consists in mixing a weighed amount of the unsaturated substance with an excess amount of peracid in chloroform solution and allowing the mixture to stand at room temperature for one-half hour; the excess peracid is then titrated in the usual manner The results are given in Table I in which the theoretical and observed values are expressed in moles of camphoric acid peracid required and moles actually used It may be seen from this table that camphoric acid peracid could be successfully used with several substances for the quantitative estimation of unsaturation Similar exceptions to those recorded in this table have been observed by Boeseken[2] and others with benzoperacid and acetoperacid.

TABLE I

THE USE OF CAMPHORIC ACID PERACID FOR THE ESTIMATION OF UNSATURATION

Substance	No. of double bonds	Moles of peracid consumed[a]	Remarks
Anethole	1	0.983	
Isosafrole	1	.979	
Isoeugenol	1	.981	
Citronellol	1	.983	
Cholesterol	1	.980	
Ergosterol	3	2.994	
Limonene	2	1.957	
d-Pinene	1	1.010	
Nonene	1	0.947	
2,4-Dimethylpentene-2	1	.972	
2,4-Hexadiene	2	.923	Only one C=C reacted
2.4-Hexadiene	2	.993	34 hours at 0°
Oleic acid	1	.997	34 hours at 0°
Linoleic acid	2	2.026	34 hours at 0°
Cinnamic acid	1	...	No measurable amount in one hour
Cinnamic aldehyde	1	0.57	34 hours at 0°
Abietic acid	1	.84	34 hours at 0°
Crotonic acid	1	.15	5 hours at room temperature
Mesityl oxide	1	.49	5 hours at room temperature

[a] Average of at least two determinations

Isolation of Products Formed by the Interaction of Camphoric Acid Peracid with Unsaturated Compounds. d-Pinene Oxide.—Five grams of d-pinene was mixed with a large excess of camphoric acid peracid in chloroform and the mixture was allowed to stand at 0° for three days It was then shaken with a 10% solution of sodium hydroxide to remove the unused peracid and camphoric acid, and finally washed with water and dried over anhydrous sodium sulfate for twenty-four hours. The chloroform solution was then removed by distillation and the remaining liquid subjected to fractional distillation under reduced pressure; the fraction distilling at 102–103° (50 mm) was collected and its physical constants determined.

TABLE II

PHYSICAL CONSTANTS OF THE PRODUCT BOILING AT 102–103° (50 MM.)

	Pinene oxide[1a] (Prileschajew)	Our product
B. p. (50 mm.)	102–103°	102–103°
d_{16}^{16}	0.9689	0.9675
n_D^{16}	1.4708	1.4740

Cholesterol Oxide.—Eight-tenths of a gram of cholesterol (Eastman Kodak c. p. product) was mixed with a large excess of camphoric acid peracid in 200 cc. of chloroform and the mixture allowed to stand at 0° for five days. The mixture was then shaken twice, each time with 200 cc. of 1 *N* sodium hydroxide solution, then with water and dried over calcium chloride. It was filtered and the chloroform removed by distillation. The residue, a white solid (m. p. 125–130°), was recrystallized three times from ethyl acetate, giving a constant melting point of 141–142°. Westphalen[6] gives a melting point of 140–141° for cholesterol oxide.

Hydrolysis of Cholesterol Oxide.—To prove definitely that our product was the oxide, 0.4 g. of the latter was heated with 4 cc. of water in a sealed tube at 115° for twelve hours. The resulting white solid was recrystallized twice from ethyl alcohol, tn. p. 239.3°. The melting point of cholestantriol has been reported by Pickard and Yates[7] and by Westphalen[6] to be 239°.

Summary

1. The stability of camphoric acid peracid and benzoperacid, in chloroform, has been measured at 0° and at 25°.

2. At 25° camphoric acid peracid is more stable, in chloroform solution, than benzoperacid, while at 0° the difference in stability is not significant.

3. Camphoric acid peracid was found to add quantitatively to certain types of unsaturated substances.

4. Pinene and cholesterol oxides have been definitely isolated from the interaction of camphoric acid peracid and *d*-pinene and cholesterol.

[6] Westphalen, Ber., 48, 1064 (1915).

[7] Pickard and Yates. J. Chem. *Soc.*, 93, 1684 (1908).

CAMBRIDGE A, MASSACHUSETTS RECEIVED JULY 20, 1932
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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

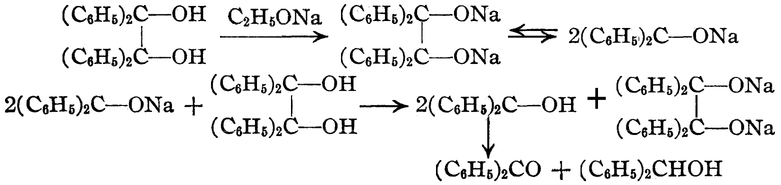
The Action of Sodium Alcoholate and of Sodium Amalgam on Aromatic Pinacols

BY W. E. BACHMANN

Reaction of Pinacols with Sodium Alcoholate.—According to Schlenk and Thal[1] sodium ketyl radicals are formed when a suspension of benzopinacol in alcohol is treated with a concentrated alcoholic solution of sodium alcoholate. We found, in agreement with Schlenk and Thal, that the deep blue color of the ketyl is produced in the reaction, but we observed further that the color disappeared completely after a short time. At first this disappearance of color was attributed to oxidation of the ketyl by oxygen of the air. That this was not the case was definitely proved when the same disappearance of color occurred when air was excluded. Hydrolysis of the colorless solution gave a mixture of equal parts of benzophenone and benzohydrol.

[1] Schlenk and Thal, Ber , 46,2841 (1913).

An insight into the mechanism of the reaction was gained by the observation that a small amount (1% by moles) of sodium alcoholate suffices to produce exactly the same phenomena: formation of the blue color followed by disappearance of the color; moreover, it was found that all of the pinacol was converted to ketone and hydrol by this small amount of sodium alcoholate. The mechanism of the reaction is considered to be the following: sodium pinacolate is formed which partly dissociates into sodium ketyl radicals; the radicals so formed then react with unchanged pinacol or with alcohol



$$\begin{array}{l}(C_6H_5)_2C{-}OH\\ \quad\ |\\ (C_6H_5)_2C{-}OH\end{array} \xrightarrow{C_2H_5ONa} \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad\ |\\ (C_6H_5)_2C{-}ONa\end{array} \rightleftarrows 2(C_6H_5)_2C{-}ONa \qquad (1)$$

$$2(C_6H_5)_2C{-}ONa + \begin{array}{l}(C_6H_5)_2C{-}OH\\ \quad\ |\\ (C_6H_5)_2C{-}OH\end{array} \longrightarrow 2(C_6H_5)_2C{-}OH + \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad\ |\\ (C_6H_5)_2C{-}ONa\end{array} \qquad (2)$$

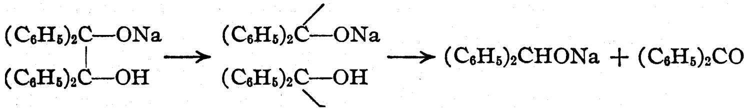
$$\downarrow$$

$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \qquad (3)$$

The products are diphenylhydroxymethyl and sodium pinacolate. The diphenylhydroxymethyl immediately disproportionates into benzophenone and benzohydrol; the sodium pinacolate can dissociate into ketyls which in turn can react with more pinacol. This mechanism satisfactorily accounts for the production and the disappearance of the color as well as for the products of the reaction. Moreover, it is clear that only a small amount of sodium alcoholate is necessary; as soon as a small amount of sodium pinacolate is produced, decomposition of the remaining pinacol is assured.

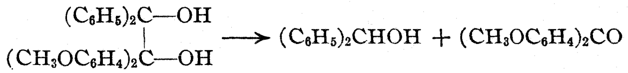
If this mechanism is correct, then according to Equation 2 a small amount of ketyl should be capable of promoting the decomposition of a large amount of pinacol. Such was found to be the case. When a small amount of ketyl was added to a solution of benzopinacol, the blue color remained for a time, then disappeared, and it was found that all of the pinacol had been converted to a mixture of ketone and hydrol. From this it follows that benzopinacol will be decomposed into a mixture of ketone and hydrol by the addition of a small amount of any sodium compound which is capable of replacing the hydrogen of the hydroxyl group by sodium.

It is not unlikely that the following reaction takes place in addition or in some cases exclusively: only one hydrogen is replaced by sodium and the mono-sodium pinacolate which results undergoes cleavage either with or without the intermediate formation of free radicals



$$\begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad\ |\\ (C_6H_5)_2C{-}OH\end{array} \longrightarrow \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \\ (C_6H_5)_2C{-}OH\end{array} \longrightarrow (C_6H_5)_2CHONa + (C_6H_5)_2CO \qquad (4)$$

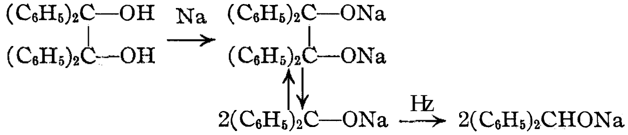
Support for this mechanism is found in the fact that the quantity of color seems less than that which would be expected if all of the pinacol passed through the ketyl stage. This second formulation would account for the results obtained with asymmetrical pinacols. When *as*-diphenyldianisylglycol reacts with sodium alcoholate the products are benzohydrol and dianisyl ketone exclusively



$$\begin{array}{l}(C_6H_5)_2C\text{—}OH \\ \quad\quad\quad\ | \\ (CH_3OC_6H_4)_2C\text{—}OH\end{array} \longrightarrow (C_6H_5)_2CHOH + (CH_3OC_6H_4)_2CO \qquad (5)$$

If the reaction proceeded according to the first formulation, one should expect the products to be benzophenone, benzohydrol, dianisyl ketone and dianisylcarbinol.

Reaction of Pinacols with Sodium Amalgam.—Linnemann,[2] the discoverer of benzopinacol, reported that benzopinacol is converted to benzohydrol when its alcoholic solution is treated with sodium amalgam and he formulated the reaction as $C_{26}H_{22}O_2 + H_2 = 2C_{13}H_{12}O$. Thorner and Zincke[3] did not believe that the pinacol was reduced directly to the hydrol in this manner; they considered that reduction to hydrol occurred only after previous cleavage of the pinacol into a mixture of ketone and hydrol. More recently, Schlenk and Weickel[4] reported that an entirely different reaction takes place. According to these investigators, hydrogen is evolved and the product is sodium ketyl $(C_6H_5)_2C\text{–}ONa$. If this reaction is correct, then hydrolysis would give a mixture of benzophenone and benzohydrol and not benzohydrol alone as Linnemann had reported. We have now found that in the reaction between benzopinacol and sodium amalgam (1.5%) in a mixture of anhydrous ether and benzene, no hydrogen is evolved; the solution becomes dark blue but after a short time nearly colorless; hydrolysis gives benzohydrol in nearly quantitative yield. Several reactions seem to be involved. In the first place, the reaction may be assumed to proceed as follows



$$\begin{array}{lcl}\begin{array}{l}(C_6H_5)_2C\text{—}OH \\ \quad\quad\ \ | \\ (C_6H_5)_2C\text{—}OH\end{array} & \xrightarrow{Na} & \begin{array}{l}(C_6H_5)_2C\text{—}ONa \\ \quad\quad\ \ | \\ (C_6H_5)_2C\text{—}ONa\end{array} \\ & & \quad\quad\ \ \uparrow\downarrow \\ & & 2(C_6H_5)_2C\text{—}ONa \xrightarrow{H_2} 2(C_6H_5)_2CHONa\end{array} \qquad (6)$$

We believe that very little of this reaction takes place. Instead, as soon as a small amount of sodium pinacolate or sodium benzohydrolate is formed, decomposition of the pinacol rapidly takes place; the mixture of benzophenone and benzohydrol so produced then reacts with the amalgam and gives benzohydrol. In support of this view it was found that if the reaction is interrupted before reduction is complete, there is obtained a mixture of pinacol, benzophenone and benzohydrol. Moreover, separate experiments showed that a mixture of equal parts of benzophenone and benzohydrol in

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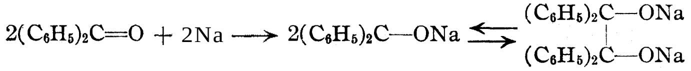
[2] Linnemann. *Ann.*, **133,** 28 (1865).

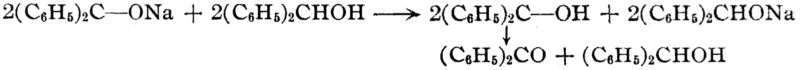
[3] Thorner and Zincke, *Ber.*, 10, 1474 (1877).

[4] Schlenk and Weickel, *ibid.*, 44, 1184 (1911).

ether and benzene reacts rapidly with sodium amalgam and gives benzohydrol; during the reduction the solution becomes dark blue in color and this color disappears when the reduction is complete. In all respects this reaction is like the reaction of the pinacol with amalgam. The deep blue color indicates that the reduction proceeds through the intermediate formation of sodium ketyl radicals and the reactions that occur are best expressed by the formulation



$$2(C_6H_5)_2C{=}O + 2Na \longrightarrow 2(C_6H_5)_2C{-}ONa \rightleftarrows \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad\;\; | \\ (C_6H_5)_2C{-}ONa\end{array} \tag{7}$$



$$2(C_6H_5)_2C{-}ONa + 2(C_6H_5)_2CHOH \longrightarrow \begin{array}{c}2(C_6H_5)_2C{-}OH\\ \downarrow \\ (C_6H_5)_2CO + (C_6H_5)_2CHOH\end{array} + 2(C_6H_5)_2CHONa \tag{8}$$

It is possible that the ketyl is reduced to some extent by the hydrogen liberated by the action of the amalgam on the benzohydrol although experiment showed that the amalgam and hydrol react very slowly with each other. Forty per cent. sodium amalgam reacts with benzopinacol in a similar manner without liberation of hydrogen; the product is nearly pure benzohydrol.

Not only benzopinacol but also substituted benzopinacols react with sodium alcoholate and with sodium amalgam. In each case the solution assumes the color characteristic of the ketyl corresponding to the ketone. In the following table are presented the results obtained by treating a number of pinacols with sodium alcoholate and with sodium amalgam.

TABLE I

ACTION OF SODIUM ALCOHOLATE AND SODIUM AMALGAM ON PINACOLS

	Sodium ethylate			Sodium amalgam	
	Color of solution	Yield, %		Color of solution	Yield, % hydrol
Pinacol		Ketone	Hydrol		
Benzopinacol	Blue	50	50	Blue	98
4,4′-Diphenylbenzopinacol	Green	50	50	Green	95
4,4′,4″,4‴-Tetraphenylbenzopinacol	Green	50	50	Green	98
Fluorenopinacol	Brown-green	50	50	Brown-green	95
4,4′,4″,4‴-Tetramethylbenzopinacol				Blue	95
as-Diphenyldianisylglycol	Blue	50	50		

Experimental

Benzopinacol (1 Mole) + Sodium Ethylate (0.1. Mole).—Although the reaction between benzopinacol and sodium ethylate takes place in alcoholic solution, the rate of reaction is slow because the pinacol is not very soluble in alcohol. As a rule a mixture of equal volumes of anhydrous ether and benzene was used. In all experiments air was excluded; this was usually accomplished by having the mixture completely fill the flask. The rate of reaction depends upon the concentration of sodium ethylate. When 0.01 mole of sodium ethylate was used for each mole of pinacol about two hours was required for decomposition of twenty grams of pinacol This time was shortened to a few minutes when 0.1 mole of alcoholate was used.

To 1 cc. of absolute alcohol contained in a 150-cc. Erlenmeyer flask was added 0.12 g. of sodium. The sodium alcoholate was dissolved in ether and benzene, 20 g. of benzopinacol was added, and the flask was then filled with solvent, stoppered and shaken. Almost immediately the solution became green and then dark blue in color; the large amount of solid pinacol disappeared; after a few minutes the color became lighter and after ten minutes the solution was colorless. Hydrolysis with dilute acid gave an oil which consisted of equivalent quantities of benzophenone and benzohydrol. It is difficult to separate this mixture quantitatively into its two components. The proportion of benzophenone in the mixture was determined by treating a portion of the oil with phenylhydrazine and estimating the amount of benzophenone-phenylhydrazone that was formed. In another portion the amount of benzohydrol was estimated in the form of the urethan formed with phenyl isocyanate.

Experiments with a number of alcoholates were carried out in a similar manner. Sodium methylate, sodium isopropylate, sodium benzohydrolate, potassium ethylate and lithium methylate induced decomposition of the pinacol. Neither magnesium methylate nor calcium methylate reacted with benzopinacol. The magnesium methylate was prepared by allowing 0.03 g. of magnesium ribbon to react with 1 cc. of methyl alcohol; the alcoholate was dissolved in 30 cc. of ether and benzene and 1 g. of benzopinacol was added. No color developed in the course of twenty-four hours and the pinacol was recovered practically unchanged. In like manner no reaction occurred when 1 g. of benzopinacol was shaken for twenty-four hours with a solution of calcium methylate which had been prepared from 0.05 g. of calcium and 1 cc. of methyl alcohol in ether and benzene.

It is now easy to interpret the results that have been reported in the past on the behavior of pinacols in the presence of alkali. Thus, Thorner and Zincke found that benzopinacol is cleaved into a mixture of ketone and hydrol by the action of a boiling alcoholic solution of potassium hydroxide. We found that the reaction between benzopinacol and an alcoholic solution of potassium hydroxide takes place readily at room temperature; in the reaction the blue color of the ketyl radicals is visible. Cohen[5] observed that complete decomposition of pinacol occurred even when small amounts of alcoholic potassium hydroxide were employed. A number of investigators have followed the directions of Thorner and Zincke; of these only Montagne and Koopal[6] report that colors are visible during the reaction. They report that benzopinacol gave a feeble blue color only when it was heated with an alcoholic solution of potassium hydroxide; tetrachlorobenzopinacol gave a blue color even at room temperature and this color disappeared on shaking the solution and then reappeared. Their failure to obtain a color with benzopinacol at room temperature as well as the loss of color on shaking the solution are attributed to oxidation of the ketyl radicals by oxygen of the air.

Benzopinacol + Sodium Ketyl.—A solution of 0.1 g of benzophenone in 20 cc. of ether and benzene was shaken with a small amount of 40% sodium amalgam which was wrapped in a piece of filter paper. As soon as the solution showed the blue color of the sodium ketyl, the amalgam was withdrawn and 1.0 g. of benzopinacol was introduced. The blue color remained as long as pinacol was present. After five minutes the colorless solution was hydrolyzed; it was found that all of the pinacol was converted to a mixture of benzophenone and benzohydrol.

Substituted Pinacols + Sodium Ethylate.—A stock solution of sodium ethylate was prepared by dissolving the alcoholate from 0.23 g. of sodium and 5 cc. of alcohol in a mixture of ether and benzene to make 100 cc. of solution. Enough of this solution was used for 1 g. of pinacol to correspond to 0.1 mole of alcoholate per mole of pinacol.

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[5] Cohen, Rec. *trav. chim.*, **38**, 72, 113 (1919).

[6] Montagne and Koopal, *ibid.*, 29, 148 (1910).

One grain of pinacol was suspended in 30 cc. of ether and benzene mixture in a test-tube and the sodium ethylate solution (3–5 cc.) was added. The solution became colored as soon as the mixture was shaken; as a rule the color disappeared after a few minutes. In most cases the mixture of ketone and hydrol was resolved into the two components by making use of the differences in solubilities of the two compounds. The yields of pure ketone and of pure hydrol which were isolated always corresponded to more than 90% of that theoretically possible.

The mixture of 4-phenylbenzophenone and 4-phenylbenzohydrol was separated by recrystallization from n-propyl alcohol; the ketone crystallizes out while the more soluble hydrol can be isolated from the liquid. 4,4′-Diphenylbenzohydrol can be easily separated from the corresponding ketone by warming the mixture with enough n-propyl alcohol to dissolve the hydrol (6 cc. per gram); the ketone is practically insoluble in the hot alcohol.

Fluorenone is readily separated from fluorenol by dissolving the mixture of the two in hot benzene; on cooling, fluorenol crystallizes out in the form of the insoluble addition compound with benzene. The mixture of benzohydrol and 4,4′-dimethoxybenzophenone which was obtained from *as*-diphenyldianisylglycol was treated with 10 cc. of 80% alcohol; this solution dissolves all of the hydrol but only a trace of the ketone. In this manner from 1 g. of pinacol there was obtained 0.55 g. (96%) of 4,4′-dimethoxybenzophenone and 0.45 g. (96%) of benzohydrol. Erdmann[7] reported that *as*-diphenyldi-*p*-tolylglycol was decomposed into a mixture of benzohydrol and di-p-tolyl ketone when it was heated with an alcoholic solution of potassium hydroxide.

When xanthopinacol was treated with a solution of sodium ethylate the solution became intensely blue in color. From the mixture xanthone but not xanthydrol was isolated in a pure state.

Benzopinacol + Sodium Amalgam (1.5%).—Three grams of benzopinacol was shaken with 65 g. of 1.5% sodium amalgam in a mixture of 30 cc. of ether and 30 cc. of benzene. In a short time the mixture was dark blue in color. After one-half hour most of the color had disappeared; after two hours the solution was nearly colorless. Hydrolysis gave 2.95 g. (98%) of pure benzohydrol. It was found that the greater part of the reaction is over in a short time. Thus, in one experiment the mixture though still colored was hydrolyzed after fifteen minutes of shaking and there was obtained a 95% yield of benzohydrol.

The substituted pinacols were allowed to react with sodium amalgam in the same manner. As a rule the mixture was hydrolyzed after being shaken for two hours. The results of these experiments are recorded in Table I.

Benzophenone + Benzohydrol + Sodium Amalgam (1.5%).—Sixty-five grams of 1.5% sodium amalgam was added to a solution of 1.50 g. of benzophenone and 1.52 g. of benzohydrol in 60 cc. of ether and benzene. After less than a minute of shaking the solution was blue in color; after one-half hour most of the color had disappeared and after two hours the solution was nearly colorless. Hydrolysis gave 2.90 g. (97%) of benzohydrol. In another experiment the solution was hydrolyzed after fifteen minutes of shaking; the yield of benzohydrol was nearly quantitative.

Benzopinacol + Sodium Amalgam (40%).—One gram of benzopinacol was added to 2.5 *g*. of 40% sodium amalgam in 15 cc. of ether and 15 cc. of benzene in a test-tube. On being shaken the mixture became dark blue in color; no hydrogen was evolved. After five minutes the blue color changed to violet and after ten minutes to violet-red. Hydrolysis gave a 94% yield of benzohydrol. Although the solution had the violet-red color characteristic of benzophenone-disodium $(C_6H_5)_2CNaONa$, only a trace of this compound was present. This was shown by passing carbon dioxide into the solution

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[7] Erdmann, Thesis, Rostock, 1910.

prior to hydrolysis; only a trace of benzilic acid was formed. Other pinacols were converted to hydrols by 40% sodium amalgam in the same manner.

When a solution of **0.50** g. of benzophenone and **0.51** g. of benzohydrol was shaken with **2.5** g. of 40% sodium amalgam in a mixture of ether and benzene, no hydrogen was evolved; the solution became dark blue and later violet red in color. Hydrolysis after fifteen minutes gave a 95% yield of benzohydrol.

The formation of the violet-red color was an indication that benzophenone is converted to benzophenone-disodium by 40% sodium amalgam. This was surprising in view of the work of Schlenk and Bergmann,[8] who showed that mercury removes one sodium from benzophenone-disodium and gives sodium ketyl. We find that a small amount of mercury removes little or no sodium and consequently 40% sodium amalgam can be used to prepare disodium derivatives of ketones. We have prepared a number of disodium derivatives by this method; in one instance, fluorenone, the disodium derivative is formed when 1% amalgam is used. The amalgam has certain advantages over the free metal and the method promises to be a convenient way of making these derivatives. Details of these experiments will be published in a future communication.

Summary

Benzopinacol and substituted benzopinacols are converted by a small amount of sodium alcoholate into a mixture of equivalent parts of ketone and hydrol. Free ketyl radicals are formed as intermediate products; these radicals are then converted by unreacted pinacol into the ketone and hydrol.

The pinacols are reduced quantitatively to hydrols by sodium amalgam in anhydrous ether–benzene solutions. This reaction, likewise, takes place through the intermediate formation of free ketyl radicals.

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[8] Schlenk and Bergmann, *Ann.*, 463, **1 (1928).**

ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND **PHYSICS** OF THE PENNSYLVANIA STATE COLLEGE]

Tertiary Aliphatic Alcohols and Chlorides Containing Normal Butyl Groups

BY FRANK C. WHITMORE AND H. MILTON WOODBURN[1]

While most alcohols are capable of rearrangement,[2] those which show this tendency to the greatest degree contain the grouping, $R_3C\overset{|}{\underset{|}{C}}OH$. Tertiary alcohols and their halides are needed for the preparation of these substances. To make such tertiary alcohols available for this work and to gain experience in handling them, this research was undertaken. The alcohols studied contain only normal aliphatic groups, including in each case at least one n-butyl group but no groups higher than butyl. All ten alcohols of this type were made and their boiling points, densities and

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree. This study was completed in July, **1930.**

[2] Whitmore, THIS JOURNAL. 54, **3274, 3431 (1932).**

refractive indices were determined under comparable conditions. Of the ten alcohols, seven have been mentioned in the literature but no adequate studies have been made with most of them. Of the ten chlorides only one, 2-chloro-2-methylhexane, has been described.[3] It was made from the carbinol by the action of hydrogen chloride or acetyl chloride.

In a few cases olefins were obtained from the carbinols or their chlorides. Preliminary studies were made on the action of bromine with some of the alcohols and on the hydrolysis of the resulting dibromides.[4]

Experimental

Preparation of the Alcohols.—All of the alcohols were made by the action of suitable Grignard reagents and carbonyl compounds.[5] These methods are summarized in Table I. The alcohols were fractionated through effective columns.[6] The higher ones were distilled under reduced pressure.

TABLE I

Carbinol	Literature preparation	Yield, %	Present method	Yield %	Yield g
Me_2Bu	$BuCO_2Et + MeMgBr$				
	$Me_2CO + BuMgBr$	92	$Me_2CO + BuMgBr$[a]	40	560
MeEtBu	$MeBuCO + EtMgI$				
	$MeEtCO + BuMgBr$	62	$MeEtCO + BuMgBr$[b]	71	480
MePrBu	$MeBuCO + PrMgI$		$MePrCO + BuMgBr$[c]	68	340
$MeBu_2$	$Ph_2CHOAc + BuMgI$		$AcOEt + BuMgBr$	65	950
Et_2Bu	$Et_2CO + BuMgBr$		$BuCO_2Et + EtMgCl$	30	30
EtPrBu			$EtPrCO + BuMgBr$[d]	52	130
$EtBu_2$			$EtCO_2Me + BuMgBr$	33	110
Pr_2Bu			$BuCO_2Me + PrMgBr$	37	90
$PrBu_2$			$PrCO_2Me + BuMgBr$	70	250
Bu_3	$Bu_2CO + BuMgBr$		$Et_2CO_3 + BuMgBr$[e]	80	280

[a] A large by-product, b. p. 100–125°, was obtained.

[b] By-products of b. p. 105–108" and 119–121°.

[c] The methyl propyl ketone was first made from acetoacetic ester ("Organic Syntheses," 1928, Vol. VIII, p. 36). As only a 20% yield was obtained, the ketone was then made by dehydrogenating (brass catalyst at 375°) methylpropylcarbinol made from methylmagnesium chloride and n-butyraldehyde (from commercial "Butalyde" supplied by the Commercial Solvents Corporation). The boiling points (at 740 mm.) of the carbinol and ketone used were 118–119° and 100.0–101.5°.

[d] Ethyl propyl ketone, b. p. 122–123" (730 mm.), was prepared in 70% yield by dehydrogenating ethylpropylcarbinol, b. p. 132–134° (730 mm.), prepared in 58% yield from ethylmagnesium chloride and butyraldehyde.

[e] During the addition of the ethyl carbonate to the Grignard solution, the latter was kept at about 30°. If cooling was used, the ethyl carbonate accumulated in the solution and later reacted violently.

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[3] Muset, Bull. *acad.* roy. *Belg.*, 775–789 (1906); Henry and de Wael, *Rec. trav. chim.*, *28*, *448* (1909); *Chem. Zentr.*, I, 7854 (1909)

[4] These results have been supplemented by W. L. Evers of this Laboratory and will be published by him.

[5] *Cf.* Edgar and co-workers, THIS JOURNAL, 51, 1483 (1929)

[6] Whitmore and Lux, *ibid.*, 54, 3451, 3453 (1932).

Properties of the Alcohols.—In determining the physical constants of the alcohols, the same apparatus and method were used throughout. All constants for a given alcohol were determined on the same sample. The boiling points were determined by actually distilling a large amount of each alcohol and taking the boiling range of the main fraction. When reduced pressure was used a barostat was employed to maintain constant pressure. The densities were determined at **20** and 25° with a bottle type pycnometer. Refractive indices were determined with an Abbé refractometer with its prism controlled by water from an automatic thermostat held at 20.0 ± 0.2°. The alcohols were all colorless. In one case, methyldibutylcarbinol, the sample became slightly yellow on standing for several weeks. The odors were pleasant. In viscosity they ranged from limpid liquids (dimethylbutylcarbinol) to thin syrups (tributylcarbinol). Table II gives the physical properties of the alcohols.

With one exception, the refractive indices increase in a fairly regular way with increasing molecular weight. Such is not the case with the densities. The properties of methyldibutylcarbinol seem to be peculiar.

TABLE II

C atoms	Carbinol	Boiling point, °C. (mm.) Literature	Boiling point, °C. (mm.) Determined	Density Literature	Density Determined d_4^{20}	Density Determined d_4^{25}	Refractive index Literature	Refractive index Detd., n_D^{20}
7	Me_2Bu	141–142 (755)	139.4–140.4 (735)	d_{20}^{20} 0.815	0.8119	0.8094	n_D 1.41592	1.4175
		58–60 (20)	53–53.5 (15)	d .8155			n_D^{20} 1.4187	
8	MeEtBu	153–160 (745)	100 (732)	d_0^{19} .8273	.8282	.8249	n_D^{19} 1.42735	1.4279
		161–162 (763)	05.2--65.8 (15)	d_4^0 .8446				
		163.5 corr.		d_4^{15} .8325				
0	MePrBu	178–183	178–9 (732)		.8267	.8237		1.4327
			78.5–79.5 (15)					
			56.2–56.4 (4)					
9	Et_2Bu	119–121 (110)	180–180.5 (733)	d_4^{20} 0.8409	,8399	.8365	n_D^{20} 1.4360	1.4362
		116–118 (105)	76.5–77.5 (15)					
10	$MeBu_2$	84–85 (10)	91.4–92.4 (15)		.8290	.8253		1.4341
10	EtPrBu		88.8–89.6 (15)		.8369	.8337		1.4378
11	Pr_2Bu		101.4–102.4 (15)		,8351	.8319		1.4390
11	$EtBu_2$		102.6–103.6 (15.5)		,8376	.8345		1.4400
12	$PrBu_2$		113.6–114.2 (15)		.8370	.8340		1.4419
13	Bu_3	120 (10)	125.0 (15)	d_4^{18} 0.844	.8408	.8368	n_D^{18} 1.4448	1.4434
		177–178 (15)	99.8–100.0 (4)					
		230–235 dec.						

Preparation and Properties of the Chlorides.—The method of Halse[7] was used. The carbinol, cooled to −10°, was saturated with dry hydrogen chloride. The halide layer was dried and freed from hydrogen chloride by standing in a vacuum desiccator over sodium hydroxide. It was also found possible to wash the chlorides with cold 5% sodium carbonate solution. In distilling the chlorides it was necessary to use a much lower pressure than with the carbinols as they are much more sensitive to heat. The decomposition appeared to be catalyzed by traces of hydrogen chloride. In such cases it was necessary to wash the chloride again with cold 5%

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[7] Halse, *J prakt Chem.*, [2] **89, 451** (1913).

sodium carbonate solution and dry it before redistilling at a lower pressure. In preparing the chlorides, deep colors often developed. These ranged from purple to black and were most noticeable with the chlorides from dimethylbutyl, methylethylbutyl and methylpropylbutylcarbinols.

The pure chlorides were colorless liquids. The odor was fainter and slightly less pleasant than that of the carbinols. There was no odor of hydrogen chloride. The pure chlorides were remarkably stable on standing. Impure samples of the chlorides darkened rapidly and gave considerable amounts of hydrogen chloride. The physical properties of the chlorides were determined as with the alcohols.

The samples were purified by distillation at reduced pressures (McLeod gage for pressures below 5 mm.) through a 30 × 1 cm. indented insulated column with complete condenser and variable take-off.[6] This arrangement was far superior to an ordinary vacuum distillation because it allowed the use of a high reflux ratio. The yields of purified products were 65–75%. The properties of the chlorides are given in Table III. Again the properties of the methyldibutyl derivative were irregular.

TABLE 111

					Stability[b]			
C atoms	Chloride	Boiling point, °C. (mm.)	Density d_4^{20}	Density d_4^{25}	Refractive index, n_D^{20}		Analysis, % Cl Calcd.	Analysis, % Cl Found
7	Me_2BuCCl	35.0–35.5 (15.5)	0.8698	0.8661	1.4205	3, 4, 5	26.37	26.2, 26.1
8	MeEtBuCCl	55.0 (15)	.8764	.8729	1.4315	3, 7, 8	23.88	24.2, 23.6, 23.7
9	MePrBuCCl	70.8–71.4 (14.5)	,8723	.8690	1.4349	6, 7, 8	21.82	21.7, 21.7, 22.2
9	Et_2BuCCl	46.0 (3)	.8856	.8822	1.4400		21.82	21.6, 21.5, 21.5
10	$MeBu_2CCl$	60.5 (3.5)	,8707	,8676	1.4382	4, 6, 8	20.09	19.8, 19.9
10	EtPrBuCCl	53–54 (2)	.8804	.8773	1.4421	4, 6, 8	20.09	20.0, 20.0
11	Pr_2BuCCl	66.5–67.5 (2.5)	,8743	.8715	1.4430	3, 4, 5	18.62	18.4, 18.4
11	$EtBu_2CCl$	69.5–70.0 (2.75)	.8784	,8756	1.4442	4, 6, 8	18.62	18.6, 18.6
12	$PrBu_2CCl$	78.8–79.2 (3)	.8736	.8715	1.4461	3, 7, 8	17.34	16.9, 17.0
13	Bu_3CCl[a]	91.5–92.5 (2.5)	.8701	.8673	1.4480	3, 4, 8	16.24	16.0, 16.0

[a] This chloride was most difficult to distil unless all traces of hydrogen chloride had been removed by long standing in the vacuum desiccator over alkali.

[b] These are the changes in the chlorides on standing for 26 months in the laboratory in ordinary bottles. 3. Slight yellow color developed. 4. No odor of hydrogen chloride. 5. Change in refractive index of about +0.001. 6. Still colorless. 7. Odor of hydrogen chloride. 8. Change in refractive index of less than +0.0004.

Preparation of Various Olefins.—In one preparation of methylethylbutylcarbinol partial dehydration took place. Five fractionations of the low boiling material gave 20 cc. with b. p. 105–108° and 125 cc. with b. p. 119–121° at 734 mm. Both reacted with bromine water to give dibromides but were not further identified.

Dehydration of 240 g. of crude methyldibutylcarbinol gave on fractionation 107 g. of olefin of b. p. 162–164° (739 mm.). The distillation of tributylcarbinyl chloride at 20 mm. gave 5-butylnonene-4,[8] b. p. 212.5–213° (735 mm.) and 60° (1.2 mm.), d_4^{20} 0.7724, n_D^{20} 1.4392.

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[8] Ivanoff, Bull. *soc. chim.*, [4] 37, 287 (1925).

Summary

1. Ten aliphatic tertiary alcohols containing n-butyl groups have been prepared and some of their properties have been determined.

2. Ethylpropylbutyl, ethyldibutyl, dipropylbutyl and propyldibutyl carbinols have been prepared for the first time.

3. The ten corresponding tertiary chlorides have been prepared and studied. All except one of these are new.

STATE COLLEGE, PENNSYLVANIA

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF MIAMI UNIVERSITY]

Alkamine Esters: Novocaine Analogs. III

BY MARLIN T. LEFFLER[1] AND HARVEY C. BRILL

In accord with the statement in a previous communication:[2] "In the absence of any considerable number of trustworthy generalizations that relate chemical structure and physiological activity, the only means of learning of the effects of such relationships are to prepare compounds of slight structural differences and study the effects of such changes," the data herewith accumulated from further studies of anesthetic compounds are presented

The anesthetic properties of the compounds that have been prepared and are herein described were determined by the use of goldfish as detailed by Adams and co-workers[3] with this slight modification, that the water used in the tests was in all cases aerated to avoid any possible effect on the fish from lack of oxygen in the water in which they were submerged.

The compounds synthesized and studied are listed below. The hydrochlorides of the esters formed by esterification of β-4-morpholinoethanol with benzoic acid, phenylacetic acid, β-phenylpropionic acid, cinnamic acid and tetrahydropyran-4-carboxylic acid, respectively; a second series of these same acids with β-N-piperidinoethanol; and a third series of esters from β-menthylethylaminoethanol with benzoic acid and tetrahydropyran-4-carboxylic acid.

Experimental

Preparation of the Alkaminoethanols.—Menthylamine was synthesized by means of the following series of reactions: menthol (U. S. P.) → menthone → menthone oxime → menthylamine. Reduction of the oxime and its recovery were carried out in accordance with the procedure detailed by Wallach and others.[4] The amine, distilled in an

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[1] Honors Student in Chemistry at Miami University, 1932.

[2] Brill, THIS JOURNAL, 54, 2484 (1932).

[3] Adams, Ridea, Burnett, Jenkins and Dreger, *ibid.*, 48, 1758 (1926).

[4] Wallach, Ann., 276, 293 (1893); Read and Story, J. *Chem. Soc.*, 2221 (1926); Read and Robertson, *ibid.*, 2209 (1926); Mailhe, Bull. *soc. chim.*, 33, 83 (1923).

atmosphere of hydrogen, boiled at 97° at a pressure of 56 mm.; yield, 75%. A mixture of equivalent amounts of menthylamine and of ethyl bromide dissolved in dry benzene was heated on a steam-bath for two hours. Precipitation of the hydrobromidc began almost immediately, so that a solid mass of crystals resulted. The free menthylethylamine distilled at 70 5° at a pressure of 4 mm.; yield 74%. β-Menthylethylaminoethanol prepared in a manner similar to the preceding synthesis was obtained in a 62% yield, boiling point 79° at 4 mm. pressure. β-N-Piperidinoethanol is best prepared by warming equivalent amounts of piperidine and ethylene chlorohydrin in the absence of a solvent in order to increase the yield of the nitrogen substituted derivative of piperidine.[5]

A number of methods were tried in the preparation of *β-4-morpholinoethanol*[6] with varying yields of morpholine and the' ethanol derivative. The results obtained are not distinctly different from those reported by Gardner and Haenni[7a] and will not be reported in detail, except to state that none were so satisfactory as the method described by the investigators just cited.

Preparation of Acids.—Tetrahydropyrancarbonic acid is the only acid used in thia study that needs any statement in regard to its preparation. The method announced by Gibson and Johnson[8] gave the best yields of those tried.[9] An attempt was made to prepare this acid by substitution of acctoacetic ester for the malonic ester with unsatisfactory results. β,β'-Dichlorodiethyl ether had not condensed completely with acetoacetic ester after refluxing for thirty-five hours and the cleavage of the condensation product did not go smoothly, consequently the effort was discontinued.

Tctrahydropyrancarbonyl chloride was prepared by heating 20 *g*. of the acid on the water-bath with 30 cc. of thionyl chloride The product distilled at 85–86° at a pressure of 16 mm.

Preparation of Esters.—In all cases the esters were produced by warrning dry benzene solutions of the various alcohols with 5% excess of like solutions of the acid chlorides until the reactions appeared to be completed.

The hydrochlorides of the esters of β-menthylethylaminoethanol apparently lose a molecule of hydrogen chloride so readily that recrystallization from alcohol and solution in water result in the production of the free base. The hydrochlorides of these esters are precipitated by the customary reactions in benzene solution; when recrystallized from alcohol–ether mixture it was found that their solubilities have changed, they are markedly more soluble in ether and hydrocarbon solvents and hardly at all soluble in water than when precipitated from the benzene solutions of the reacting base and acid chlorides. Their melting points have changed and they give no test for chlorine A portion of the ester of tetrahydropyran-4-carbonic acid was recrystallized from dry ether before this sensitiveness to alcohol and water had been observed. The melting point of this is reported in Table II. As this melting point is lower than that for the free base and the

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[5] Powell and Dehn, THIS JOURNAL, 39, 1717 (1917).

[6] Kamm and Waldo, *ibid.*, 43, 2223 (1921); Cretcher and Pittenger, *ibid.*, 47, 163 (1925).

[7] (a) Gardner and Haenni, *ibid.*, 53, 2763 (1931). (b) The authors wish to express their appreciation to the Carbide and Carbon Chemicals Corporation for their gift of the triethanolamine used in this investigation.

[8] Gibson and Johnson, J. *Chem. Soc.*, 2525 (1930).

[9] V. Braun and Koehler, *Ber.*, 50, 1057 (1917).

TABLE I

SOME DATA ON CERTAIN ALKAMINE ESTERS

	Hydrochlorides	Formula	Yield, %	M. p., °C.	Chlorine, % Calcd.	Chlorine, % Found
A.	β-4-Morpholinoethylbenzoate	$C_{13}H_{17}NO_3HCl$	48	205	13.06	12.85
B.	β-4-Morpholinoethylphenylacetate	$C_{14}H_{19}NO_3HCl$	45	131	12.42	12.26
C.	β-4-Morpholinoethyl-β-phenylpropionate	$C_{15}H_{21}NO_3HCl$	73	139	11.84	11.63
D.	β-4-Morpholinoethylcinnamate	$C_{15}H_{19}NO_3HCl$	65	211	11.92	11.68[a]
E.	β-4-Morpholinoethyl-tetrahydropyran-4-carbonate	$C_{12}H_{17}NO_4HCl$	75	145	12.68	12.53
F.	β-N-Piperidinoethyl benzoate	$C_{14}H_{19}NO_2HCl$	64	176	13.15	13.02
G.	β-N-Piperidinoethyl phenylacetate	$C_{15}H_{21}NO_2HCl$	95	139	12.50	12.39
H.	β-N-Piperidinoethyl-β-phenylpropionate	$C_{16}H_{23}NO_2HCl$	65	116	11.91	11.79
I.	β-N-Piperidinoethylcinnamate	$C_{16}H_{21}NO_2HCl$	76	158	11.99	11.76
J.	β-N-Piperidinoethyl-tetrahydropyran-4-carbonate	$C_{13}H_{23}NO_3HCl$	50	103	12.78	12.69

[a] A Dumas nitrogen determination gave 4.78% found, 4.71% calculated. These esters have the usual solubility in water and alcohol with less solubility in ether, acetone and chloroform and decidedly less solubility in benzene and petroleum ether. They were recrystallized from a mixture of alcohol and ether.

TABLE II

DATA ON CERTAIN MENTHYLAMINE DERIVATIVES

	B. p., °C.	M. p., °C.
Menthylamine	97 (56 mm.)	
Menthylethylamine	70.5 (4 mm.)	(HBr) 306 (decomp.)
β-Menthylethylaminoethanol	79 (4 mm.)	(HCl) 274 (decomp.)

		Formula			Calcd., %	Found, %
K.	β-Menthylethylaminoethylbenzoate	$C_{21}H_{33}NO_2$	155	N	4.23	4.26
L.	β-Menthylethylaminoethyltetrahydropyran-4-carbonate	$C_{20}H_{37}NO_3$	166	N	4.13	4.25
M.	Hydrochloride	$C_{20}H_{37}NO_3HCl$	142[a]	Cl	9.73	8.23

[a] The melting point and the chlorine content of this ester indicate that a small portion of hydrogen chloride has been lost even though this compound has been recrystallized from dry ether and has been protected from moisture and alcohol.

TABLE III

ANESTHETIC EFFECTS ON GOLDFISH AND PH VALUES

Compound hydrochlorides	PH[a] 0.006 mol. concn.	Mole concn., used	Time in sol?., min.	Observed effect	Fate after removal
β-4-Morpholinoethylbenzoate	4.4	0.006	45	Sluggish, incomplete anesthesia	Recovered
		.024	25	Irritated, evidences of toxicity	Died
β-4-Morpholinoethylphenylacetate	4.4	.024	25	Irritated, evidences of toxicity	Died
β-4-Morpholinoethylphenylpropionate	4.3	.012	60	Sluggish, incomplete anesthesia	Recovered
β-4-Morpholinoethylcinnamate	4.4	.006	45	Very sluggish, incomplete anesthesia	Recovered
		.012	11	Complete anesthesia	Recovered
β-4-Morpholinoethyltetrahydropyran-4-carbonate	4.4	Not tested			
β-N-Piperidinoethylbenzoate	6.4	.006	45	Sluggish, incomplete anesthesia	Recovered
		.024	25	Sluggish, evidences of toxicity	Recovered
β-N-Piperidinoethylphenylacetate	5.9	.006	31	Very sluggish. incomplete anesthesia	Recovered
		.012	45	Very sluggish, no marked increase in effect	Recovered
β-N-Piperidinoethyl-β-phenylpropionate	4.8	.012	45	Very sluggish, incomplete anesthesia	Recovered
β-N-Piperidinoethylcinnamate	6.4	.003	69	Very sluggish, incomplete anesthesia	Recovered
		.005	54	Complete anesthesia	Recovered
		.006	10	Complete anesthesia	Recovered
		.007	9	Complete anesthesia	Recovered
		.008	10	Complete anesthesia	Recovered
		.012	7	Complete anesthesia	Recov. with difficulty
β-N-Piperidinoethyltetrahydropyran-4-carbonate	4.8	.008	30	Slight sluggishness	Recovered
		.012	30	Greater sluggishness	Recovered

K, L and M could not be tested for reasons already noted.

[a] The PH values were found by means of a Hellige comparator.

percentage of chlorine found is likewise low, it is apparently a mixture of the hydrochloride and the basic ester free of hydrogen chloride. Solutions of these basic esters in dry benzene or ether did not form precipitable hydrochlorides or hydrosulfates when dry hydrogen chloride and sulfuric acid, respectively, were added under the conditions used.

Their study is being continued and they will be reported upon in more detail later.

Surface Tension Relationships.—The surface tensions of three of these esters, namely, the hydrochlorides of β-N-piperidinoethylcinnamate (the most active anesthetic of those studied), β-4-morpholinoethylcinnamate (ot intermediate activity) and β-N-piperidinoethyl-β-phenylpropionate (of low activity) were determined. The results of these tests show so little differences in values that no conclusion can be drawn as to the influence of surface tension on the anesthetic powers of the compounds. The compound with the highest anesthetic effect has the highest surface tension instead of the lowest as would be expected from Traube's theory. Certainly the chemical constitution appears to be one of the more important factors in the establishment of physiological activity as Adams has noted in his study of the relationships between surface tension and bactericidal activity.[10]

TABLE IV

SURFACE TENSIONS AND DENSITIES (0.006 MOLAR CONCENTRATIONS), 25°

Compound, hydrochlorides	Density of solution	Surface tension, dynes/cm.
β-N-Piperidinoethylcinnamate	0.9965	71.96
β-4-Morpholinoethylcinnamate	.9969	69.30
β-N-Piperidinoethyl-β-phenylpropionate	.9969	69.00
Redistilled water	.9970	71.80

Discussion and Conclusions.—The menthyl derivatives were included in this investigation in the hope that they might show marked surface penetration because of their high radical weight and favorable configuration. Rather convincing evidence of this relationship is furnished by the marked surface penetrating power of cocaine and of the greater activity of Butyn[11] over Novocaine in this regard. The former two are more penetrating and of higher molecular weight than the last named anesthetic.

The morpholine esters are not as active anesthetics as the piperidine esters. This structure appears to have no advantage over other basic groups in endowing compounds with anesthetic powers. They are likewise somewhat more acid in properties, and high acidity in local anesthetics appears to be undesirable and unfavorable to the best results. For this same reason the esters of tetrahydropyran-4-carboxylic acid are likely to possess low activity. This configuration apparently has no pronouncedly unfavorable toxic effect on compounds.

[10] Stanley and Adams, THIS JOURNAL, 54, 1548 (1932).

[11] Schmitz and Loevenhart, J. *Pharmacol.*, 24, 167 (1924).

The cinnamates are the most active of all studied, which is evidence of the favorable effect of a double bond in enhancing the anesthetic powers of compounds.

Summary

1. Esters of β-4-morpholinoethanol with benzoic, phenylacetic, β-phenylpropionic, cinnamic and tetraphydropyran-4-carboxylic acids; a second series of β-N-piperidinoethanol with these same acids; and a third series of β-menthylethylaminoethanol with benzoic and tetrahydropyran-4-carboxylic acids are described under the following heads: (a) preparation, (b) physical properties, (c) PH values, (d) anesthetic activities, (e) surface tension.

2. The cinnamates are the most active physiologically of those studied.

3. No apparent relationship between surface tension and surface penetration was indicated.

4. The menthylethylamino derivatives differ from the others studied in the ease with which hydrogen chloride is lost.

OXFORD, OHIO

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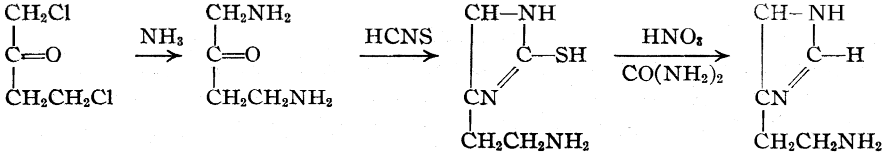
α′,β-Dichloromethylethyl Ketone (1,4-Dichlorobutanone-2)[1]

BY R. H. CARROLL AND G. B. L. SMITH

Introduction

The preparation of α′,β-dichloromethylethyl ketone is not recorded in the literature, and this relatively simple substance is important because of the possibility of using it as an intermediate in the synthesis of compounds of biological and pharmacological interest. For instance it might be employed in the synthesis of histamine, as follows[2]



The present paper describes two methods for the preparation of α′,β-dichloromethylethyl ketone.

The Nierenstein Reaction.—In 1915, Clibbens and Nierenstein[3] reported that acid chlorides react with diazomethane to produce α-chloro

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[1] This paper is constructed from part of the thesis submitted by Mr. Carroll to the faculty of the Polytechnic Institute of Brooklyn in June, 1932, in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Now being investigated in this laboratory.

[3] Clibbens and Nierenstein, J. *Chem. Soc.*, 107, 1491 (1915).

ketones, but Bradley and Robinson[4] in employing this reaction obtained instead the diazo ketone. Bradley and Robinson[5] and Bradley and Schwarzenbach[6] found that when one molecular equivalent of an acid chloride is allowed to react with two molecular equivalents of diazomethane, the diazo ketone is obtained in excellent yields. Bradley and Schwarzenbach[6] were able to obtain the a-chlor ketone from the diazo ketone by treatment of the latter substance with dry hydrogen chloride.

α′,β-Dichloromethyl ethyl ketone was prepared through the Nierenstein reaction from diazomethane and β-chloropropionyl chloride and subsequent treatment of the product with dry hydrogen chloride. The α′,β-dichloromethylethyl ketone was identified by analysis and by the preparation of the hydrochloride of a new thiazole, 4-(β-chloroethyl)-2-aminothiazole. The ketone itself was a strong lachrymator. It distils at 65° at 3 mm. and changes from a colorless to a brown liquid on standing. Its specific gravity 20°/4° is 1.3295 (±0.0005)

Condensation of Ethylene and Chloroacetyl Chloride with Aluminum Chloride.—Lippmann[7] in 1864 prepared β-chloropropionyl chloride from ethylene and phosgene. This reaction suggested that if chloroacetyl chloride were used instead of phosgene, a',@-dichloromethylethylketone might be formed. Various condensation agents such as mercuric sulfate, sulfuric acid, stannic chloride and aluminum chloride were used to bring about this reaction between chloroacetyl chloride dissolved in diethyl ether and ethylene, the ethylene being passed into the ethereal solution. These attempts were not successful.

Petroleum oils have been condensed[8] by the use of the addition compound of ethylene and aluminum chloride. Accordingly this ethylene–aluminum chloride addition compound was prepared in a dry petroleum ether solution and chloroacetyl chloride was added. α′,β-Dichloromethylethyl ketone was obtained in small yield and it was identified through the condensation product with thiourea."

Experimental

Materials.—Diazomethane was prepared by the method of von Pechman[10] using nitrosomethyl urethan.[11] The ether was dried over sodium, distilled, dried over phosphoric anhydride and redistilled. β-Chloropropionic acid was prepared by the method given by Powell in "Organic Syntheses."[12] β-Chloropropionyl chloride[13] was prepared

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(4) Bradley and Robinson, J. *Chem. Soc.*, 1545 (1928).

(5) Ref. 4, p. 1310.

(6) Bradley and Schwarzenbach, *ibid.*, 2904 (1928).

(7) Lippmann, Ann., **129**, 81 (1864).

(8) British Patent 345,334, Dec 18. 1930; see *Chem. Abstracts*, **26**, 155 (1932).

(9) See Popp. Ann., 150, 274 (1889); Hantzsch, *ibid.*, 249, 1, 7, 31 (1888); **250**, 257 (1889); Näf, *ibid* , **265**, 108 (1891); Traumann, *ibid.*, **249**, 31 (1888).

(10) Houben-Weyl, "Methoden der organischen Chemie," G. Thieme, Leipzig, v. 3, 2d ed., 1922, p. 124.

(11) Purchased from the Eastman Kodak Company.

(12) "Organic Syntheses," John Wiley and Sons, Vol. VIII, 1928, p. 58.

(13) See Michael, Ber.. 84, 4048 (1901), also Wolfenstein and Rolle, *ibid.*, 41, 736 (1908).

by heating together a mixture of 15 g. of β-chloropropionic acid and 18 g. of thionyl chloride for ninety minutes. The mixture was fractionated at 5 mm.; 13 g. was collected at 44°, b. p. 144°.

α',β,-Dichloromethylethyl Ketone (1,4-Dichlorobutanone-2) through the Nierenstein Reaction.—4.75 grams of β-chloropropionyl chloride was dissolved in 25 g. of absolute ether and the solution was cooled to −5°; 1.8 g.[14] of diazomethane was dissolved in 75 g. of absolute ether contained in a 500-ml. suction flask, cooled to −5°, and protected from moisture by a calcium chloride tube. This solution was treated with the ethereal solution of β-chloropropionyl chloride, taking about five minutes for the addition The temperature was maintained at −5° and the solution was allowed to stand for one hour, at the end of which period a second portion of 1.8 g. of diazomethane was added to the solution, nitrogen being again evolved. The solution was now placed in an ice box and allowed to stand for thirty-six hours. The yellow colored solution was treated with dry hydrogen chloride until the color was pale yellow and the evolution of nitrogen had ceased. During the treatment with hydrogen chloride the temperature was held below 10". The ether was evaporated by a current of dry air and the residue was fractionated at reduced pressure. The portion distilling at 65° under a pressure of 3 mm. was collected; yield 3.2 g. The liquid had powerful lachrymatory properties and the density was 20°/4°, 1.3295. Refractive index [n_D] 1.480 at 20°; molecular refraction calcd., 30.59; found, 30.10. This sample was two weeks old and a sample two months old gave a value [n_D] 1.473 at 20°.

Anal. Calcd. for $C_4H_6OCl_2$: C, 34.04; H, 4.25. Found: C, 34.29; H, 4.09.

This preparation was repeated using 22 g. of β-chloropropionyl chloride and 14.4 g. of diazomethane; yield 18 g. at 65° and 3 mm. pressure.

Hydrochloride of 4-(β-Chloroethyl)-2-aminothiazole.—2.8 Grams of α', β-dichloromethylethyl ketone was added to a solution of 1.4 g. of thiourea in 25 ml. of water and' heated on the water-bath under reflux for thirty minutes. The mixture was frequently agitated and at the end of this period the insoluble layer of the ketone had entirely disappeared. The solution was evaporated under reduced pressure to 15 ml. and then made alkaline by adding 20 ml. of a solution of 0.1 *N* sodium hydroxide. It was then extracted with diethyl ether and the ethereal solution was dried with anhydrous sodium sulfate. The ether was evaporated and the residue crystallized; yield 1.4 g.; m. p. 60°. This base could not be recrystallized readily and accordingly the hydrochloride salt was prepared.

One-half gram of 4-(β-chloroethyl)-2-aminothiazole base was dissolved in 20 ml. of absolute ether and filtered; 20 ml. of absolute ether was saturated with dry hydrogen chloride and this was added to the solution of the base. The crystals which separated were filtered, washed with absolute ether, and dried *in vacuo* over calcium chloride and paraffin. The substance, m. p. 166°, started to melt at 144" but then solidified. The analyses were made on reprecipitated material.

Anal. Calcd. for $C_5H_8N_2SCl_2$: C, 30.15: H, 4.02; S, 16.08. Found: C, 31.01, 31.11; H, 4.56, 4.54; S, 16.62.

α',β-Dichloromethylethyl Ketone from Ethylene and Chloroacetyl Chloride.—Two hundred and fifty ml. of dry petroleum ether (b. p. 40–60°) was placed in a three-necked flask fitted with a mechanical stirrer and a reflux condenser which was protected against moisture with a tube of calcium chloride, and 13.3 g. of powdered aluminum chloride (Akatos) was added. Ethylene was passed into the solution for two hours while the solution was maintained at the boiling temperature (47°) and most of the aluminum chloride dissolved; 11.3 grams of chloroacetyl chloride was added slowly through a separatory funnel and the mixture was boiled for thirty minutes after the addition of

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[14] Determined by titration by the *p*-nitrobenzoic acid method

the chloroacetyl chloride. The mixture was poured into 600 ml. of ice water and stirred until the aluminum chloride had decomposed. The layer of petroleum ether was separated and the aqueous solution was extracted three times with a total volume of 300 ml. of diethyl ether. The combined extract was dried with anhydrous sodium sulfate, evaporated by a current of dry air and fractionated under reduced pressure. The fraction distilling at 63–65° under **3** mm pressure was collected; yield 2 8 g.

0.14 Gram of this product and 0.076 g. of thiourea ucre dissolved in 4 ml. of water and heated for thirty minutes. The solution was made alkaline with a solution of sodium hydroxide and extracted with ether. The residue remaining after the evaporation of the ether melted at 60°. A mixed melting point determination of this material with the previously prepared thiazole base gave no depression. The hydrochloride of this substance was prepared as previously described, it melted at 166" and showed a tendency to fuse at 140° after which it solidified. This substance gave no depression in a mixed melting point determination with 4-(β-chloroethyl)-2-aminothiazole hydrochloride prepared from the larger sample of α',β-dichloromethylethyl ketone. These facts are taken as positive proof that aluminum chloride can be used as a condensing agent for the preparation of this ketone.[15]

Summary

1. α',β-Dichloromethylethyl ketone, 1,4-dichlorobutanone-2, has been prepared by the action of diazomethane on β-chloropropionyl chloride and subsequent treatment with dry hydrogen chloride.
2. α',β-Dichloromethylethyl ketone has been prepared by the direct addition of ethylene to chloroscetyl chloride, using aluminum chloride as a condensing agent.
3. 4-(β-Chloroethyl)-2-aminothiazole has been prepared from a',β-dichloromethylethyl ketone and thiourea. The hydrochloride of this base was identified by analysis.
4. Mixed melting point determinations have been used to identify the α',β-dichloromethylethyl ketone prepared from ethylene and chloroacetyl chloride.

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[15] **This reaction will be studied further in this Laboratory as a means of preparing chloro ketones.**

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on Acid Iodides. I. The Preparation of Halogen Substituted Aliphatic Acid Iodides with a Note on the Atomic Refractivity of Iodine

BY EDWIN L. GUSTUS AND PHILIP G. STEVENS

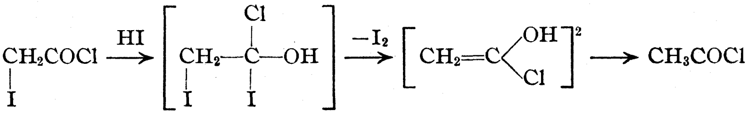
Knowledge of the chemistry of acid iodides is very meager. The difficulties of their preparation, their reactivity and instability doubtless are responsible for the neglect which this group of substances has received. We have been attracted to their study through the hope that their reactivity might make them useful as reagents for achieving unusual chemical transformations.

This paper, the first of a series, deals with the preparation of certain halogen substituted aliphatic acid iodides, and the determination of some of their physical constants.

The most satisfactory method for the preparation of acid iodides is that of Staudinger and Anthes,[1] who prepared acetyl, diphenylacetyl and benzoyl iodides by passing a stream of dry hydrogen iodide into the corresponding acid chloride. This method proved to be very successful for the preparation of chlorinated acid iodides. In this way, monochloro-, dichloro- and trichloroacetyl iodides were easily prepared from the corresponding acid chlorides.

Bromoacetyl chloride was also converted into the corresponding iodide, but attempts to obtain it in a pure form were unsuccessful. It failed to crystallize at --80°, and when warmed to 32° during an attempt at distillation it decomposed with the evolution of heat, forming large amounts of a black crystalline solid, presumably iodine monobromide.

Attempts to prepare iodoacetyl iodide failed completely, as iodine was instantly liberated, even at $-10°$. This was not surprising, however, as the following set of reactions suggests.



$$\underset{\text{I}}{\text{CH}_2}\text{COCl} \xrightarrow{\text{HI}} \left[\underset{\text{I}}{\text{CH}_2}\text{—}\overset{\text{Cl}}{\underset{\text{I}}{\text{C}}}\text{—OH}\right] \xrightarrow{-\text{I}_2} \left[\text{CH}_2\text{=C}\begin{matrix}\text{OH}\\ \text{Cl}\end{matrix}\right]^{2} \longrightarrow \text{CH}_3\text{COCl}$$

The following table is a summary of the physical constants of these acid iodides.

Iodide	B. p , °C.	Mm.	d^{20}_{4}	d^{20}_{20}	n^{20}_{D}	Condition at $-80°$
CH_3COI	104–106	735	2.0674	2.0710	1.5491	Not crystalline
CH_2ClCOI	36.5	4	2.2607	2.2647	1.5903	Crystalline
$CHCl_2COI$	54–54.5	15	2.2508	2.2547	1.5754	Not crystalline
CCl_3COI	74–74.2	30	2.2549	2.2589	1 5711	Crystalline
CH_2BrCOI	32°, dec.					
CH_2ICOI	Below $-10°$, dec.					

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[1] Staudinger and Anthes, *Ber.*, 46, 1417 (1913)

[2] Compare Aschan, *ibid.*, 45, 1913 (1912).

No determination of the atomic refractivity of iodine in the form of acid iodide has been thus far reported. For this reason the densities and refractive indices of the iodides were determined where possible. The atomic refractivity of iodine as acid iodide has been calculated from the molecular refractivity of acetyl iodide.

Iodide	M_D observed	M_D calculated for CH_3CO	Atomic refractivity I^{-CO-}
CH_3COI	26.08	10.35	15.73

Using this value for iodine, the exaltation of the molecular refractivity, EM_D, has been calculated for the chloroacetyl, dichloroacetyl and trichloroacetyl groups as acid iodides. The exaltation was found to be negative in each case.

Iodide	M_D observed	M_D calculated	EM_D
CH_2ClCOI	30.52	30.94	−0.42
$CHCl_2COI$	35.08	35.81	− .73
CCl_3COI	39.83	40.68	− .85

For purposes of comparison, the atomic refractivities of chlorine, bromine and iodine are shown.

Halogen X	A X^{-CO-}	B X^{-CH_2-}	A − B	A ÷ B
Cl	6.336^3	5.9673	0.369	1.0618
Br	9.595^4	8.748^4	0.847	1.0968
I	15.73	13.900^3	1.83	Calcd. 1.133^5; found, 1.131

We wish to express our thanks to Dean Frank C. Whitmore for the facilities of this Laboratory, and to the Mallinckrodt Chemical Works for so generously donating the large quantities of iodine necessary for this work. Part of the funds required for this research were privately contributed.

Experimental Part

Acetyl Iodide, CH_3COI.—This substance, b. p. 104–106° (735 mm.), was prepared from purified acetyl chloride by the method of Staudinger and Anthes.[1] These workers, however, submitted no analyses or physical constants other than the boiling point. The iodide did not solidify at −80° (solid carbon dioxide and alcohol). When shaken with mercury, it became colorless.

Anal. (PdI_2) Calcd. for C_2H_3OI: I, 74.69. Found: I, 74.44.

Chloroacetyl Iodide, CH_2ClCOI.—198 grams of chloroacetyl chloride, b. p. 105–106" (740 mm.), cooled to −5°, was treated with 672 g. of dry hydrogen iodide. The resulting reddish liquid was fractionated *in vacuo*.

1st fraction b. p. 30–36.5° (4 mm.)	40 g.	
2d fraction b. p. 36.5° (4 mm.)	245 g.	68% yield
3d fraction b. p. 36.5–37.5° (4 mm.)	25 g.	

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(3) Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911).

(4) Karvonen, *Ann Acad Sci. Fennicae, AS*, 62 (1914)

(5) Calculated from above two ratios.

The second fraction, b. p. 36.5" (4 mm.) was a heavy, mobile, highly refractive, cherry red liquid of penetrating odor, fuming strongly in moist air. It could be obtained colorless by shaking with mercury, but the red color rapidly returned even if protected from the light at 0°. The iodide sinks in water and, due to its slight solubility, reacts rather slowly to form chloroacetic and hydriodic acids. It dissolves without reaction in the laboratory hydrocarbons, chloroform and carbon tetrachloride. It dissolves in alcohol, reacting instantly with the formation of ethyl chloroacetate. It is soluble in ether and slowly reacts with it, forming ethyl iodide and ethyl chloroacetate. When cooled to −80° the iodide solidified to a mass of colorless leaflets. When shaken with mercury, it became colorless.

Anal. (PdI_2). Calcd. for C_2H_2OClI: I, 62.12. Found: I, 62.39

Dichloroacetyl Iodide, $CHCl_2COI$—Seventy grams of dichloroacetyl chloride, b. p. 106.1–107.1° (739 mm.), was treated with 192 *g.* of dry hydrogen iodide at −5°. The resulting golden-yellow liquid was distilled *in oacuo.* The distillate, b. p. 50–58° (14 mm.), was then fractionated.

1st fraction b. p. (15 mm.)	50–54	27 g.	
2d fraction b. p. (15 mm.)	54–54.5°	66 g.	58.2% yield
3d fraction b. p. (15 mm.)	54.5–58°	15 g.	

The second fraction, b. p. (15 mm.) 54–54.4°, entirely resembles chloroacetyl iodide in appearance, properties and solubilities. It reacts, however, much more slowly with ethers. It failed to crystallize at −80". When shaken with mercury. it became colorless.

Anal. (PdI_2). Calcd. for C_2HOCl_2I: I, 53.13. Found: I, 53.60.

Trichloroacetyl Iodide, CCl_3COI.—The preparation of this substance was previously reported by Gal,[6] who obtained a low yield of doubtless impure material from the reaction of an excess of phosphorus triiodide with trichloroacetic acid. It is easily prepared by the action of hydrogen iodide on trichloroacetyl chloride. 100 g. of trichloroacetyl chloride, b. p. (726 mm.) 116–117°, was treated with 220 g. of dry hydrogen iodide at −5°. The resulting dark red liquid was freed from dissolved iodine by distillation *in vacuo* from mercury, and then fractionated.

1st fraction b. p. (30 mm.)	below 74°	31.2 g.	
2d fraction b. p. (30 mm.)	74--74.2"	107.5 g.	71.5% yield

The second fraction, b. p. (30 mm.) 74–74.2°, resembles in appearance and' solubilities the other chlorinated acid iodides, but it is less sensitive to light, and reacts more slowly with water. The most marked difference, however, is its inability to cleave ethers. It solidifies readily at −80° to colorless leaflets. When shaken with mercury, it became colorless.

Anal. (PdI_2). Calcd. for C_2OCl_3I: I, 46.44. Found: I, 46.41.

From the first fraction, after decomposition with water, was obtained a small quantity of an inert liquid with an odor of carbon tetrachloride, b. p. 77–102° (735 mm.), which was not further investigated.

Bromoacetyl Iodide, CH_2BrCOI.—One hundred grams of bromoacetyl chloride, b. p. (737 mm.) 125.0–125.3°, prepared by the method of Hans Meyer[7] was treated with 244 g. of dry hydrogen iodide at −5°. The liquid rapidly became dark brown. When about one half of the hydrogen iodide had been bubbled in, noticeable amounts of a black crystalline material commenced to precipitate. At the end, the deep reddish

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(6) Gal, *Bull. soc. chim.*, [2] *20*, 13 (1873).

(7) Hans Meyer, *Monalsh.*, 22, 418 (1901).

liquid was decanted from the black precipitate. This crystalline substance gave strong tests for both iodine and bromine, and was possibly a mixture of iodine monobromide and iodine. After unsuccessfully trying to purify the decanted liquid by freezing out crystals of bromoacetyl iodide, an attempt was made to distil it in *vacuo.* When the bath temperature reached 32°, the liquid suddenly decomposed with the evolution of considerable heat, and the formation of large amounts of the black crystalline material mentioned above.

Iodoacetyl Iodide, CH_2ICOI.—Spindler[8] attempted to prepare this substance by heating chloroacetyl chloride with calcium iodide in a sealed tube. The method of Staudinger and Anthes proved to be equally unsuccessful. Fifty grams of freshly redistilled iodoacetyl chloride, b. p. 31–32° (4 mm.), prepared by the method of Abderhalden and Guggenheim[9] was placed in a gas wash bottle and cooled to –10°. When dry hydrogen iodide was passed into the liquid, there was an instantaneous precipitation of iodine crystals completely stopping the passage of the gas. Evidently iodoacetyl iodide, if formed, is unstable at –10°.

Summary

1. The method of Staudinger and Anthes for the preparation of acid iodides has been extended to include the preparation of several halogenated aliphatic acid iodides.

2. Chloro-, dichloro- and trichloroacetyl iodides have been prepared by this method, and some of their physical constants and chemical properties have been determined.

3. Bromoacetyl iodide has been prepared, but it was too unstable to permit purification by distillation.

4. Iodoacetyl iodide could not be prepared.

5. The atomic refractivity of iodine as acid iodide, and the exaltation of molecular refractivity for chloro-, dichloro- and trichloroacetyl iodides have been determined.

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(8) Spindler, Ann., 231, 274 (1885).

(9) Abderhalden and Guggenheim, Ber., 41, 2853 (1908).

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on Acid Iodides. II. The Cleavage of Aliphatic Ethers by Acid Iodides

BY EDWIN L. GUSTUS AND PHILIP G. STEVENS

It has long been known that aliphatic ethers may be cleaved by acid chlorides at elevated temperatures in the presence of catalysts.[1] Recently it has been shown that the reaction proceeds at ordinary temperatures, though very slowly.[2] With acid chlorides it has not been possible to dispense with a catalyst.[3] Acid bromides, however, cleave ethers without the use of catalysts, though high temperatures are required to accomplish this result.[4]

More than twenty years ago Kishner[5] observed that benzoyl iodide was able to cleave ethers readily at 100° without a catalyst, forming alkyl iodides and benzoates. Since this isolated observation has not received the further investigation which its suggestive character would indicate, we have undertaken a comprehensive study of the reaction between acid iodides and ethers with the hope not only of developing a useful method for the investigation of ethers, but also of adding to our knowledge of the mechanism of the reaction between acid halides and ethers.

Due to the sluggishness of the reaction between benzoyl iodide and ethers, requiring a temperature of 100° for several hours, we have directed our attention to aliphatic acid iodides[6] with the hope that they would prove more reactive and that transformations with them might be obtained at ordinary temperatures. Thus the detrimental effect of elevated temperatures on unstable substances would be eliminated. This expectation has been entirely fulfilled.

When an aliphatic ether is treated with acetyl iodide, the reaction mixture becomes warm after a short induction period of often less than **a** minute. This heat, which we believe is due to the formation of an oxonium complex, is soon dissipated. If the mixture is allowed to stand at room temperature for two to five days, it is found that the ether has been cleaved with the formation of an alkyl iodide and an alkyl acetate. This reaction was found to proceed much faster with di-secondary ethers than with di-primary.

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(1) For a review of the literature see Meerwein and Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932).

(2) Norris and Rigby, THIS JOURNAL, **54**, 2093 (1932).

(3) Descudé, *Compt. rend.*, **132**, 1129 (1901).

(4) Lydén, *Finska Kemistsamfundets Medd.*. **35**, 19–36 (1926); **37**, 53–71 (1928); **38**, 19–46 (1929); **38**, 72–84 (1929). *Chem. Abstracts*, **22**, 3880 (1928); **23**, 1868 (1929); **24**, 336 (1930); **24**, 1628 (1930).

(5) Kishner, *J. Russ. Phys.-Chem. Soc.*, **41**, 651–659 (1909); *Chem. Zentr.*, **2**, 1132 (1909). Compare also Blaise, *Compt. rend.*, **139**, 1211 (1904); **140**, 661 (1905); Staudinger and Anthes, *Ber.*, **46**, 1423 (1913).

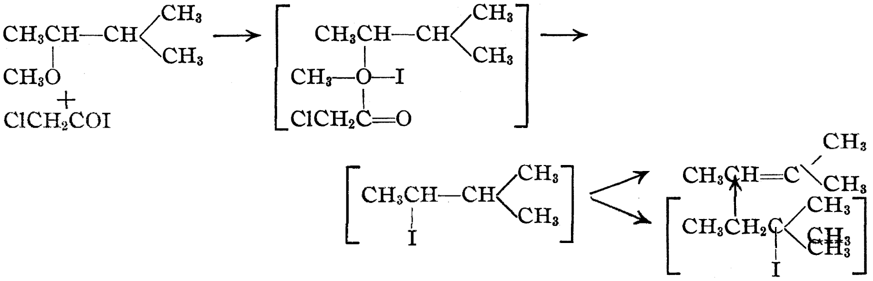
(6) Gustus and Stevens, THIS JOURNAL, **55**, 374 (1933).

After this work had been completed, a paper by Meerwein and Maier-Hüser[1] appeared in which these workers suggested the oxonium salt mechanism in the case of the acid iodides. Meerwein and Maier-Hiiser, however, were not the first to use such a mechanism. Kishner,[5] the first to study ether cleavages by acid iodides, had already considered oxonium complex formation as a preliminary step to cleavage.

The molecular weight of primary ethers appears to influence slightly the ease with which they are cleaved. Thus the cleavage of di-n-propyl, di-n-butyl and diisoamyl ethers by acetyl iodide proceeds less readily as the molecular weight of the ether increases.

The introduction of chlorine into the ether molecule in the a-position was found to affect greatly its stability toward acid iodides. Thus chloroacetyl iodide, which cleaves ordinary ethers readily, caused no cleavage of sym-dichlorodimethyl ether in twenty-five days at room temperature followed by six days at 100°. There was here no apparent evidence of oxonium complex formation. Possibly no oxonium complex formed, thus prohibiting cleavage.

The cleavage of unsymmetrical aliphatic ethers by acid iodides was also investigated. It was found with di-primary ethers that the greater proportion of iodine attached itself to the smaller alkyl group. This confirms Kishner's[5] observation with benzoyl iodide and is in accord with the work of Norris and Rigby[2] with acid chlorides. With mixed primary–secondary ethers about one-half of the iodine went to the smaller (in this case the primary) radical. In addition rearrangement products appeared. Thus the methyl ether of methylisopropylcarbinol with chloroacetyl iodide formed methyl iodide and trimethylethylene in about equal quantities. The latter substance may have come from methylisopropyliodomethane, or from tertiary-amyl iodide, a rearrangement product[7]



Norris and Rigby[2] have already shown that methyl isobutyl ether and acetyl chloride in the presence of zinc chloride form mainly isobutyl chloride with some tertiary-butyl chloride, a rearrangement product.

Acid iodides are practically always contaminated with dissolved iodine. It was thought that this substance might be acting as a catalyst in ether

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(7) Compare Wischnegradski, Ann., 190, 342 (1878).

cleavages. For this reason attempts were made to cleave ethers with acetyl chloride using iodine as a catalyst. After long standing at room temperature, no evidence of any reaction could be found.

The structure of the acid iodide in ether cleavage reactions is almost as important as the structure of the ether itself. The introduction of chlorine into the iodide has a marked effect. Thus chloroacetyl iodide was found to cleave ethers less readily than acetyl iodide, and dichloroacetyl iodide was very much less reactive. Definite evidence of a reaction between trichloroacetyl iodide and either primary or secondary ethers at room temperature could not be obtained. The same result was observed when zinc iodide was used as a catalyst. It is probable that an oxonium complex was first formed in each case, for heat was liberated when the iodide and ether were mixed. This was particularly noticeable with diisopropyl ether, but no cleavage took place. A very small amount of cleavage possibly occurred with diethyl ether at 100° after three hours. This failure of trichloroacetyl iodide to cleave ethers cannot be attributed to the lack of a hydrogen atom in the α-position to the carbonyl group since benzoyl iodide, which has no a-hydrogen atom, is able to cleave them.

Acid iodides not only cleave oxygen ethers, but thioethers as well. This was not unexpected for Cahours[8] had already reported the cleavage of thioethers by acid bromides at elevated temperatures, and had mentioned that acid iodides behaved similarly, though more vigorously. He failed, however, to report any experimental evidence. Owing to the criticism of his work by Obermeyer,[9] and the doubtful purity of the acid iodide available to him, this unsupported statement required further investigation.

While thioethers are cleaved by acid iodides, the rate of cleavage is very much slower than that of oxygen ethers. The cleavage products, in the case of diethyl sulfide, were ethyl iodide and ethyl thiolacetate. This slower cleavage may be due to the fact that the —S—C bond is in general stronger than the —O—R bond. Acetyl chloride without catalysts failed completely to cleave diethyl sulfide after seven days at 100°.

One of the most reactive ethers is ethylene oxide. Little work has been done on its reaction with acid halides.[10] Ethylene oxide reacts so vigorously with halogen acids that reactions with acid halides might be easily misinterpreted as true cleavages by the halide rather than as a chain reaction caused by small amounts of halogen acid present. Acetyl iodide reacts very vigorously with ethylene oxide even at $-80°$, and the reaction is so rapid that it seems quite reasonable to suppose true cleavage takes place. The product is β-iodoethyl acetate. The reaction with acetyl chloride was also tried, using acetyl chloride which had been freed from hydrogen chloride by distillation from dimethylaniline. Precautions were

(8) *Cahours, Bull. soc. chrm.,* [2] **25, 563 (1876)**; *Compt.* **rend., 81, 1163 (1876).**

(9) *Obermeyer, Ber.,* **20, 2921 (1887).**

(10) Bodforss, *Ahrens Sammlung, 26,* **221 (1920)**; *Altwegg* and *Landrivon, U. S. Patent* **1,393,191.**

taken to exclude all moisture. There was no apparent reaction at −80° nor at room temperature. After forty-four days, the material was fractionated directly. The yield of β-chloroethyl acetate was about 90%.

A similar experiment was made with acetyl chloride and ethylene oxide in the presence of a small amount of iodine. Here considerable heat was evolved at the outset. After three and a half days at room temperature, the yield of β-chloroethyl acetate was about 30%. If instead of iodine one drop of concentrated hydrochloric acid was used, the yield of β-chloroethyl acetate after two and a half days was about 75%. From these experiments it appears as if acetyl chloride may slowly cleave this very reactive ether without a catalyst at room temperature. A further investigation of this reaction, however, is now in progress.

When equivalent quantities of ethylene oxide, acetyl chloride and iodine were mixed at —SO°, at first no reaction occurred. The sealed tube containing the reaction mixture, now dark brown from dissolved iodine, was removed from the freezing mixture and shaken in the daylight. About fifteen seconds later, the tube exploded with great violence, although still at a low temperature. The formation of an iodo-hypoiodite at −80° reasonably accounts for the detonation.[11]

Although aromatic ethers, such as diphenyl ether and diphenylene oxide are unattacked by hydriodic acid even at 250°,[12] they were found to react vigorously with acetyl iodide at room temperature. This reaction will be made the subject of a future communication.

Though all acetyl iodides form oxonium complexes with ethers, the progressive introduction of chlorine decreases their ability to cleave ethers. The formation of a complex is, therefore, no criterion of subsequent cleavage. Halogen substitution apparently stabilizes the oxonium complex in some way not yet understood.

If the acid halides are compared with the hydrogen halides in regard to their reactivity toward ethers,[13] it will be seen that acid chlorides resemble hydrogen chloride. Since hydrogen halides, acid bromides[14] and iodides do form oxonium complexes with ethers, it is not unreasonable to suppose that acid chlorides may also do so, though to a very much less extent. The metal or non-metal halide used with acid chlorides as a catalyst for ether cleavage may greatly facilitate the formation of the oxonium complex, but it seems to us that the important role of the catalyst is rather the promotion of the decomposition of this complex.

We wish to express our thanks to Dean Frank C. Whitmore of the School of Chemistry and Physics of the Pennsylvania State College for laboratory

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(11) Compare Birckenbach and Goubeau, Ber., 65B, 397 (1932); Maass and Boomer, THIS JOURNAL, 44, 1709–1721 (19'22).

(12) Hoffmeister, Ber., 3, 747 (1870).

(13) Hantzsch, ibid., 54B, 1851 (1921).

(14) Based on the fact that acid bromides cleave ethers without catalysts at elevated temperatures

facilities, to the Mallinckrodt Chemical Works for so generously donating the large quantities of iodine consumed in this research, and to E. I. du Pont de Nemours, Inc., for kindly contributing the dimethyl ether used in our experiments. Part of the funds required for this research were privately contributed.

Experimental Part

Acetyl Iodide and Di-n-propyl Ether.—12.25 grams (0.12 mole) of di-n-propyl ether, b. p. 89–90.2' (from metallic sodium) was treated with 17 g. (0.10 mole) of acetyl iodide. The usual warming of the mixture was noticed, and the tube was allowed to stand protected from light at 25°. After eighty-nine hours, the reaction mixture was shaken with a saturated sodium carbonate solution, and 50 cc. of diisoamyl ether was added. After drying over anhydrous potassium carbonate, the solution was cooled, treated with 10 g. of anhydrous trimethylamine, and allowed to stand for twelve days at 25°, and then for six days at 65°. At the end of this time the solution was repeatedly washed with water, and the washings evaporated in *vacuo* over sulfuric acid; 10.5 g. of trimethyl-*n*-propylammonium iodide was obtained, which separated as platelets from absolute alcohol. The diisoamyl ether extract, after drying, was fractionated twice, finally yielding 0.45 g. of n-propyl acetate.

The following reactions were carried out in essentially the same way as described for n-propyl ether. Those marked with an asterisk are described in detail.

Iodide	Ether	Ammonium iodide	M. p., °C.	Yield, %	Acetate	B. p., °C. (730 mm. ±)	n_{D}^{20}	Hours
Acetyl	Dimethyl	Trimethylphenyl	210–211	88.2	Methyl	55 – 56.6	1.3636	240
	Di-n-propyl	Trimethyl-n-propyl	185–186	45.8	n-Propyl	100 –102	1.3839	89
	Di-n-butyl	Trimethyl-n-butyl	230–231	45.2	n-Butyl	126 –130	1.3969	89
	Diisoamyl	Trimethylisoamyl	193–194	41.2	Isoamyl	139.2–141.2	1.4054	89
	Diisopropyl	Trimethylisopropyl	285–286	73.1	Isopropyl	87 – 88	1.3954	89
	*Diethyl sulfide	Triethyl sulfonium cadmium iodide double salt	154	13.2	Ethyl thiol	See text		1296
	*Ethylene oxide			73.8	β-Iodoethyl	95 – 96 (43 mm.)	1.5072	20 ±
Chloro-acetyl	*Diethyl	Dimethylethyl-phenyl	135–136	90.9	Ethyl chloro	141.6–141.9	1.4217	120
Dichloro-acetyl	Diethyl	Dimethylethyl-phenyl	135–136	24.6	Ethyl dichloro	150 –152	1.4308	144
Trichloro-acetyl	*Diisopropyl	No reaction						168

Acetyl Iodide and **Diethyl** Sulfide.—37.5 grams of acetyl iodide was treated with 70.5 g. of diethyl sulfide in the usual way. After twenty days, golden-yellow crystals of triethylsulfonium iodide began to separate. After fifty-four days the reaction mixture was shaken well with water, the aqueous layer separated, and the non-aqueous layer shaken for twenty-four hours with water to convert any ethyl iodide into the soluble triethylsulfonium iodide. This aqueous layer was separated, added to the previously obtained washings, and the whole neutralized with dilute sodium hydroxide. There was a large amount of acid, indicating much unreacted acetyl iodide. The neutralized solution was concentrated in *vacuo* to about 150 cc., filtered hot and treated with an excess of hot, filtered, half-saturated cadmium iodide solution. After twelve hours at 0°, the sparingly soluble crystalline double salt, $[(C_2H_5)_3SI]_2CdI_2$, was collected, washed with water and alcohol and air dried. It weighed 25 g., corresponding to 4.54 g. of ethyl iodide. It melted at 119–120° and showed no depression when mixed with a known sample which had been recrystallized from dilute cadmium iodide solution.

When recrystallized from alcohol, it melted at 154°[15] and showed no depression when mixed with a known sample, also from alcohol. It lost no weight in drying at 110° and 20 mm.

Anal. Calcd. for $C_{12}H_{30}S_2I_4Cd$: I, 59.13. Found: I, 58.95.

The non-aqueous portion consisted of excess dicthyl sulfide and ethyl thiolacetate. As it was impossible to separate these two compounds by distillation, the diethyl sulfide was removed by diluting with diethyl ether, shaking up with water and excess methyl iodide until the aqueous extracts gave no precipitate of $[CH_3(C_2H_5)_2SI]_2CdI_2$ with cadmium iodide solution.[16] The ether extract, having the odor of ethyl thiolacetate, was dried and fractionated. The residue, boiling above 92°, was converted into ethyl mercaptochloride for identification according to the method of Sachs.[17] The ethyl mercaptochloride was recrystallized from a large volume of boiling xylene, separating in the form of characteristic hexagonal plates. It was dried at 110° and 20 mm.

Anal. (micro Carius). Calcd. for C_2H_5SHgCl: S, 10.79. Found: S, 10.70.

Acetyl Iodide and Ethylene Oxide.—Sixty-two grams of acetyl iodide, dissolved in an equal volume of carbon tetrachloride, was placed in a strong Pyrex tube, and the solution was frozen and cooled to —80°, carefully excluding moisture. An excess (20 cc.) of ethylene oxide was distilled in, and the tube sealed and shaken in the freezing bath. As soon as the reaction started, the frozen layer began to melt, and in a few moments complete mixing had occurred. The reaction proceeded with the liberation of much heat, as evidenced by the rapid vaporization of the carbon dioxide from the cooling bath. Within five minutes, the violence of the reaction had subsided, and the contents of the tube consisted of a dark, mobile liquid. After standing overnight at 25°, the tube was opened and the excess ethylene oxide allowed to evaporate. The reaction product, examined in the usual way, was fractionated *in vacuo.*

1st fraction	b. p. (43 mm.) 90–95°	2.4 g.	73.8% yield
2d fraction	b. p. (43 mm.) 95–96'	46.7 g.	
Residue		8.5 g.	

The second fraction, β-iodoethyl acetate, had a sharp, fruity odor, and its vapor attacked the eyes. When colorless the refractive index was n^{20}_{D} 1.5072.

Anal. (PdI_2). Calcd. for $C_4H_7O_2I$: I, 59.30. Found: **1,** 58.99.

Acetyl Chloride and Ethylene Oxide.—25.3 grams of acetyl chloride, freshly distilled from dimethylaniline, was treated with 18 g. of dry ethylene oxide. There was no obvious reaction at —80° nor at 25°. After standing for forty-four days at 25°, the excess of ethylene oxide (contaminated with acetaldehyde) and unreacted acetyl chloride were removed at 25° *in oacuo* and the residue fractionated, the second fraction being practically pure β-chloroethyl acetate.

1st fraction	b. p. (733 mm.) up to 142.4°	n^{20}_{D} 1.4215	2.5 g.	95.7% yield
2d fraction	b. p. (733 mm.) 142.4–143.8"	n^{20}_{D} **1.4235**	29.0 **g.**	
Residue		n^{20}_{D} 1.4333	6.3 g.	

Acetyl Chloride, Ethylene Oxide and Hydrochloric Acid.—25.3 grams of the same pure acetyl chloride, 18 g. of dry ethylene oxide, and one drop of concentrated hydrochloric acid were treated exactly as in the preceding experiment but for only two and a half days.

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[15] Compare Ray, Adhikari and Banerjee, J. *Indian Chem. Soc.*, 8, 739 (1931); *Chem. Abstracts*, 26, 3199 (1932).

[16] Procedure suggested by Mr. J. M. Herndon of this Laboratory.

[17] Sachs, *Ber.*, **54B**, 1851 (1921).

1st fraction b. p. (732 mm.) 138–143°	n^{20}_{D} 1.4229	6.0 g.	77.9% yield
2d fraction b. p. (732 mm.) 143–144°	n^{20}_{D} 1.4240	18.8 g.	
Residue	n^{20}_{D} 1.4316	6.0 g.	

Acetyl Chloride, Ethylene Oxide and **Iodine.**—"A," 25.3 g. of the same pure acetyl chloride was treated with 18 g. of dry ethylene oxide and 10 mg. of resublimed iodine. At −80° there was no apparent reaction but on warming to room temperature the iodine dissolved, giving the solution a brown color, which, however, soon disappeared. The tube became slightly warm and remained so for several minutes. After three and a half days at 25° the material was treated exactly as before.

1st fraction b. p. (723 mm.) 138–143°	n^{20}_{D} 1.4235	3.5 g.	31.3% yield
2d fraction b. p. (723 mm.) 143–144°	n^{20}_{D} 1.4242	3.5 g.	
Residue	n^{20}_{D} 1.4401	5.4 g.	

"B," 26.5 g. of the same pure acetyl chloride was treated with 17.5 g. of dry ethylene oxide and 38.6 g. of dry, powdered, resublimed iodine. After sealing, the tube was removed from the cooling bath and shaken without protection from light. After fifteen seconds the tube exploded with great violence.

Acetyl Chloride, Diisoamyl Ether and Iodine.—Eighteen cc. of the same pure acetyl chloride was treated with 25 cc. of diisoamyl ether and 15 mg. of resublimed iodine. The iodine color slowly disappeared. After 44 days at 25°, the contents of the tube were examined in the usual way. The diisoamyl ether was recovered unchanged, and no evidence of cleavage of the ether could be found.

Chloroacetyl Iodide and **Diethyl** Ether.—Fifty-six grams of chloroacetyl iodide was treated with an excess (44 g.) of diethyl ether in the usual way. After five days, the products were carefully fractionated:

1st fraction b. p. (736 mm.) 36–71.7°	n^{20}_{D} 1.4524	7.2 g.
2d fraction b. p. (736 mm.) 71.7–72.2°	n^{20}_{D} 1.5077	28.5 g.
3d fraction b. p. (736 mm.) 72.2–74°	n^{20}_{D} 1.5098	4.9 g.
4th fraction b. p. (736 mm.) 74–141.6°	n^{20}_{D} 1.4292	8.0 g.
5th fraction b. p. (736 mm.) 141.6–141.9°	n^{20}_{D} 1.4217	19.5 g.
Residue	n^{20}_{D} 1.4262	4.0 g.

The second and third fractions were practically pure ethyl iodide, further identified by conversion into dimethylethylphenylammonium iodide. The **fifth** fraction, as shown by analysis and physical constants, was pure ethyl chloroacetate.

Anal. (micro). Calcd. for $C_4H_7O_2Cl$: C, 39.18; H, 5.76. Found: C, 39.30; H, 5.85.

The total yield of ethyl iodide was 90.9% and of ethyl chloroacetate 92.2%.

Chloroacetyl Iodide and n-Butyl Methyl Ether.—Forty-five grams of chloroacetyl iodide was treated with 22 g. of n-butyl methyl ether, b. p. (737 mm.) 69.8–70° (from metallic potassium). On mixing, the usual increase in temperature was noticed. After two weeks the contents of the bulb were partially fractionated to obtain the methyl iodide formed.

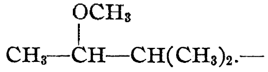
1st fraction b. p. (729 mm.) 42–43°	22.6 g.
2d fraction b. p. (729 mm.) 43–75°	12.0 g.

The residue was then treated to remove any acetyl iodide, dried and fractionated.

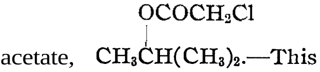
3d fraction b. p. (727 mm.) 72–111°	n^{20}_{D} 1.4325	1.0 g.
4th fraction b. p. (727 mm.) 111–135°		4.4 g.
5th fraction b. p. (727 mm.) 135–178.2°	n^{20}_{D} 1.4522	4.9 g.
6th fraction b. p. (727 mm.) 178.2–179°	n^{20}_{D} 1.4313	17.4 g.
Residue		4.8 g.

The first fraction, consisting of practically pure methyl iodide, and the second fraction were converted into trimethylphenylammonium iodide, giving 42 5 g. of the salt, m. p. 211–12°, 73.2% yield. The fourth fraction was n-butyl iodide, identified as trimethyl-n-butylammonium iodide, m. p. 230°, yield 13.3%. The sixth fraction was pure n-butyl chloroacetate.

Chloroacetyl Iodide and Methylisopropylcarbinol Methyl Ether.—Forty-five grams of chloroacetyl iodide was treated with 25 *g.* of methylisopropylcarbinol methyl ether. The usual increase in temperature was noticed on mixing. After sixteen days the tube was opened and the low boiling products were fractionated off directly: 36.5 g. of material, b. p. (731 mm.) 33–53°, was obtained. Floating on this distillate was about 0.5 g. of water. At present it is not possible to account definitely for the formation of water in this reaction. The distillate was diluted with benzyl alcohol, washed with dilute sodium carbonate, dried and treated with an excess of freshly distilled dimethylaniline. After standing for twenty-four hours the trimethylethylene was fractionated from this mixture; 13.9 g. of material, b. p. (730 mm.) 33–36°, was obtained which had the odor of trimethylethylene, reacted instantly with bromine in carbon tetrachloride without the formation of hydrogen bromide and gave a copious yellow precipitate with Denigès' reagent.[18] The trimethylphenylamrnoninm iodide in the residue was precipitated with benzene, collected and washed with petrolic ether; wt. 20 *g.*, m. p. 208°, 33.5% yield. The original residue from which the methyl iodide and trimethylethylene had been distilled was so decomposed that no homogeneous material could be isolated from it.

Preparation of Methylisopropylcarbinol Methyl Ether,  $CH_3—\overset{OCH_3}{\overset{|}{C}H}—CH(CH_3)_2$.—132 grams of methylisopropylcarbinol, b. p. (734 mm.) 111–112°, dissolved in 800 cc. of pure *p*-cymene, was treated with a large excess (120 g.) of bright potassium shot. The material, after six hours on the steam-bath, was boiled for two hours. After cooling, 340 g. of redistilled dimethyl sulfate was slowly added. When the reaction had subsided, the reaction mixture was boiled for twelve hours and fractionated several times, yielding 86 g. of pure methylisopropylcarbinol methyl ether, b. p. (737 mm.) 81.2–81.5°, d_{20}^{20} 0.7600, d_4^{20} 0.7586, n_D^{20} 1.3850.

Anal. (micro). Calcd. for $C_6H_{16}O$: C, 70.51; H, 13.82. Found: C, 70.45; H, 13.78.

Preparation of Methylisopropylcarbinol Chloroacetate,  $CH_3\overset{OCOCH_2Cl}{\overset{|}{C}}H(CH_3)_2$.—This substance was an expected cleavage product from methylisopropylcarbinol methyl ether, but was not thus obtained. It was prepared from the carbinol with chloroacetyl chloride in benzene solution and potassium carbonate, b. p. (738 mm.) 180–181°, d_{20}^{20} 1.0437, d_4^{20} 1.0418, n_D^{20} 1.4298.

Anal. (micro). Calcd. for $C_7H_{13}O_2Cl$: C, 51.05; H, 7.96. Found: C, 51.15; H. 8.20.

Chloroacetyl Iodide and *Sym*-dichlorodimethyl Ether.—Fifty grams of chloroacetyl iodide was treated with 31.25 g. of sym-dichlorodimethyl ether, b. p. (736 mm.) 101.2–101.5". The usual increase in temperature on mixing was not noticed. After twenty-five days, a small sample was withdrawn. It reacted with water and dissolved completely, indicating that no reaction had occurred. The tube was re-sealed and heated to 100° for six days. On re-examination, large amounts of unchanged acid iodide and sym-dichlorodimethyl ether were found, and no material insoluble in water save a little separated iodine was observed. Since the products expected, chloroiodomethane which is insoluble in water, and chloromethyl chloroacetate which reacts slowly with water and

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(18) Denigès, *Compt. rend*, 126, 1145, 1277 (1898).

is Sparingly soluble, were obviously absent, it was concluded that no reaction had taken place.

Trichloroacetyl Iodide and **Diethyl** Ether.—32.7 grams of trichloroacetyl iodide was treated with an excess (23.3 g.) of diethyl ether. There was a very slight increase in temperature on mixing. After one hundred and twelve hours, the reaction products were examined in the usual way, but only unchanged diethyl ether was recovered, and no evidence of any cleavage could be found. A similar result was obtained with one gram of zinc iodide dissolved in the reaction mixture.

Trichloroacetyl Iodide and Diisopropyl Ether.—Thirty grams of trichloroacetyl iodide was treated with 12 g. of diisopropyl ether. On mixing there was a very considerable increase in temperature. After seven days at 25°, the contents of the tube were examined in the usual way. Diisopropyl ether was recovered, and no evidence of any cleavage of the ether was observed. Another tube containing, in addition, 1 g. of zinc iodide gave a similar result. In this case, however, practically all of the zinc iodide remained undissolved.

Trichloroacetyl Iodide and Diethyl Ether at 100°.—Twelve grams of trichloroacetyl iodide was treated with 4 g. of diethyl ether and heated to 100° for three hours. On working up the material in the usual way, about 0.2 cc. of a heavy liquid with a fruity odor was obtained which gave qualitative tests for both chlorine and iodine. While too small in amount to permit separation and purification of the components, it probably consisted of ethyl trichloroacetate and ethyl iodide, contaminated with unchanged diethyl ether. It is possible that a slight amount of cleavage of the ether took place.

Summary

1. The reactions between acetyl iodide and dimethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether, diisoamyl ether, diethyl sulfide and ethylene oxide have been studied.

2. The reactions between chloroacetyl iodide and diethyl ether, n-butyl methyl ether and methylisopropylcarbinol methyl ether have been studied.

3. The introduction of chlorine into acetyl iodide has been found to diminish progressively its ability to cleave ethers, trichloroacetyl iodide being unable to cleave ethers at room temperature.

4. Di-secondary ethers react much more rapidly with acid iodides than di-primary ethers. Increasing the molecular weight of di-primary ethers decreases slightly the rate of cleavage.

5. Sym-dichlorodimethyl ether could not be cleaved by chloroacetyl iodide.

6. No reaction was observed at room temperature between primary ethers and acetyl chloride in the presence of dissolved iodine.

7. No reaction was observed between diethyl sulfide and acetyl chloride after one week at 100°.

8. The reaction between acetyl chloride and ethylene oxide has been studied.

9. The preparation and some physical constants of methylisopropylcarbinol methyl ether and methylisopropylcarbinol chloroacetate have been described.

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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

Levulinic Acid. IV. The Vapor Pressures of its Normal-Alkyl Esters (C_7-C_{10})

BY MILFORD A. COWLEY AND H. A. SCHUETTE

In an earlier study[1] of the temperature–vapor pressure relationships of an homologous series of alkyl esters of levulinic acid, questions arose concerning the preparation and the stability of its higher members in the region of their boiling points. In order to obtain more information about members of this series and to test the validity of a formula, at that time presented, for calculating the specific gravities of the normal alkyl esters, the n-heptyl, n-octyl, n-nonyl and n-decyl esters were prepared and certain of their simpler physical properties determined as before. Because the work has been temporarily halted, it seems desirable to record now the data that have been obtained.

Experimental

Preparation of the Esters.—Levulinic acid (n^{40} 1.4342) was directly esterified with the appropriate alcohol[2] (molecular ratio of acid to alcohol, 1.1 to 1) using as a catalyst hydrogen chloride in the amount of 3% of the weight of the alcohol. Carbon tetrachloride served the dual role of solvent for the reactants and of agent for the removal of water from the reaction mixture by means of a continuous separator. Although the higher alcohols themselves are sufficiently insoluble in water to make possible their use as separating agents, such procedure is undesirable because of the high boiling temperature of the alcohols and the inevitable waste of such valuable reagents.

As was previously found in the cases of the n-amyl and n-hexyl esters, complete separation of the higher esters from the excess levulinic acid was not accomplished by a single fractional distillation under reduced pressure. Satisfactory removal of the acid from the ester fraction of the first distillation was brought about by shaking the mixture with dry, powdered sodium carbonate (6 to 8 g. of Na_2CO_3 to 50 g. of ester). Water was added dropwise with thorough shaking after each addition. The close approach of neutrality was indicated when the sodium carbonate particles agglomerated and settled as a granular mass. Although this mode of procedure for neutralizing the ester fraction proved effective, yet it was observed that the addition of water in excess of the amount needed to bring about this change

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[1] Schuette and Cowley, THIS JOURNAL, 53, 3485 (1931).

[2] The alcohols, with one exception, were Eastman products. They were distilled before use. n-Decanol was prepared for us in the laboratory of Professor Homer Adkins by B. H. Wojcik, who hydrogenated ethyl n-caprate over a copper-chromium-barium oxide catalyst [Folkers and Adkins, *ibid.*, 54, 1145 (1932)]. Their assistance is gratefully acknowledged.

in appearance of the carbonate is to be avoided, otherwise troublesome emulsions form. The neutral esters, without exception, were again fractionated under reduced pressure. Molecular refractions, computed by the formula of Lorenz and Lorentz, were used as a measure of the purity of the final product.

The properties of the esters so prepared are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OR LEVULINIC ACID ESTERS

Alkyl	n^{20}	Specific gravity (20°/4°)	Molecular refraction (Lorenz–Lorentz) Obs.	Calcd.
n-Heptyl	1.4360	0.94332	59.365	59.391
n-Octyl	1.4380	.93635	63.754	63.994
n-Nonyl	1.4400	.93360	68.386	68.597
n-Decyl	1.4417	.92653	73.141	73.200

Specific Gravities.—Elsewhere[1] the suggestion was made that the specific gravities of the higher (liquid) members of this homologous series might be predicted with fair accuracy by means of the empirical formula $488.18d^2 - 1029.1d + 543.34 = c$, in which d and c represent specific gravity and number of carbon atoms in the alkyl radical, respectively. This was, however, not found to be the case with respect to all of the four new esters herein described for, with the exception of the n-heptyl derivative, each showed a deviation above the predicted value which is too large to be disregarded. Obviously the mathematical expression in question has a very limited use for predicting by extrapolation the specific gravities of the higher esters ($C_7 - C_{10}$). A better summation of the data at hand for the ten normal esters is given by the expression

$$d = 0.868686 + 0.772094/(c + 3.29699),$$

in which d and c have the same significance as in the preceding formula. The deviations will in no case exceed three-tenths of one per cent. when this formula is applied to these ten esters.

Vapor Pressures.—The isoteniscopic method of Smith and Menzies[3] was used for the determination of vapor pressures because it is more economical of material and more sensitive to the decomposition of these esters than is the dynamic method of Ramsay and Young.[4] Pressures were read from a closed manometer which had been checked against a standard barometer. Temperatures were determined by means of a two-junction, iron–constantan thermopile in connection with an accurate potentiometer and a reflecting galvanometer. The thermopile was calibrated against Bureau of Standards thermometers over the temperature range of the experiments. The isoteniscope bulb was suspended in a well-insulated air-bath provided with a carefully controlled electrical heating

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[3] Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

[4] Ramsay and Young, J. Chem. *Soc.*, 47, 42 (1885).

unit, a rapid stirrer and a small observation window. Maintaining the temperature constant to ±0.1° for a period of one-half minute was sufficient to allow for lag in the temperature-measuring device. Pressures are accurate to ±0.2 mm.; temperatures to ±0.2°.

Temperature–pressure relationships are expressed by means of the Kirchhoff[5] formula (Table II).

TABLE II

PRESSURE–TEMPERATURE RELATIONSHIPS OF LEVULINIC ACID ESTERS

Alkyl	Log P	B. p. (760 mm.), calcd. °C.
n-Heptyl	$19.3441-3.4634 \log T-3876.49/T$	283.5
n-Octyl	$16.9838-2.5904 \log T-3938.57/T$	291.1
n-Nonyl	$13.0149-1.2273 \log T-3855.21/T$	298.0
n-Decyl	$28.5652-6.0977 \log T-5120.54/T$	306.5

Discussion

That the esters decompose to form more volatile compounds upon heating was demonstrated by several observations. Vapor pressure data obtained for isobutyl levulinate by the static method[3] showed values in excellent agreement in the lower temperature range with those previously found by the dynamic method,[4] but definite deviations above those determined by the dynamic procedure were observed as the temperature was raised and the time of heating prolonged (Fig. 1). That this phenomenon may be indicative of decomposition has been noted in the case of *n*-valerolactone.[6] The beginning of the deviation is so definite that it recommends this method of dual determinations as a means of ascertaining the temperature at which decomposition begins. Data obtained for the new esters by the static method show at elevated temperatures similar high pressure values that cannot be made to conform to the Kirchhoff formula. Besides this, substantiation of this conclusion was found in the fact that a test run using n-octyl levulinate that had been once used for a vapor pressure determination gave high pressure values throughout the entire temperature range. Furthermore, it may not be without significance that all of the esters turned from colorless to yellow during the runs, the color being more intense at the surface exposed to the air.

The inconsistent pressure values (near atmospheric pressure) were disregarded in the formulation of the equations (Table II). The effect of decomposition is, therefore, to produce only a slight modification of the slope of the equation in the region of high pressure, which tends to make the calculated values for the boiling points slightly low and the values for the heats of vaporization and molar entropies slightly high.

Although the purified esters were kept in brown bottles protected from the light, they appeared to decompose partially upon standing. A fraction

[5] Kirchhoff, Ann. *physik. Chem.* (*Poggendorf*), 103,185 (1858).

[6] Schuette and Thomas, THIS JOURNAL, 52,2028 (1930).

more volatile than the freshly prepared ester was obtained upon redistillation, the refractive index was lowered and the esters assumed a faint yellow color after a period of weeks. For this reason, freshly distilled material was used in the vapor pressure measurements.

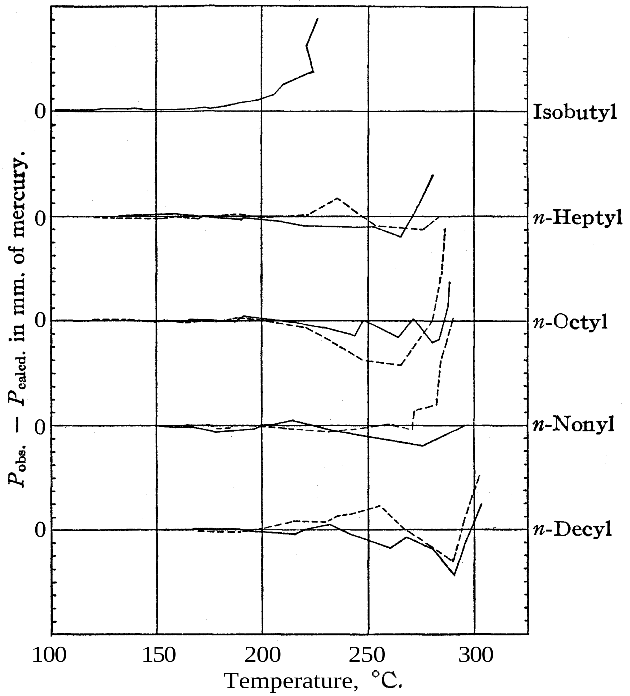

Fig. 1.—Deviation between observed and calculated vapor pressures of alkyl esters of levulinic acid. Ordinate graduations represent 10-mm. intervals; duplicate runs are indicated by unbroken and broken lines, respectively.

The excess of the molar entropies (Table III) over the average value of 27.3 given by Hildebrand[7] for normal liquids, is due in part to the result of decomposition though there is no apparent reason to suspect that the excess is not due partially to association of the liquids since all of the lower esters showed entropy values above the normal figure.

TABLE III

ENTROPIES OF VAPORIZATION OF THE ALKYL LEVULINATES

Alkyl	Temperature, °A.	Molar heat of vaporization (cal. mole)	Entropy of vaporization
n-Heptyl	496.2	14339.0	28.9
n-Octyl	507.2	15559.5	30.7
n-Nonyl	515.9	16341.8	31.7
n-Decyl	524.4	17210.0	32.8

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[7] Hildebrand, THIS JOURNAL, 37, 970 (1915).

Summary

Four new esters of levulinic acid have been prepared and characterized by some of their physical properties. Evidence has been presented to show that these esters decompose at their boiling points near atmospheric pressure.

MADISON, WISCONSON RECEIVED JULY 28, 1932
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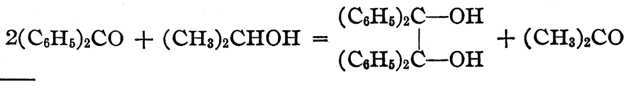
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OP MICHIGAN]

The Photochemical Reduction of Ketones to Hydrols

BY W. E. BACHMANN

It has recently[1] been shown that a small amount of sodium alcoholate can effect the decomposition of a large amount of benzopinacol into a mixture of benzohydrol and benzophenone. It occurred to us that through this reaction it should be possible to obtain hydrols by photochemical reduction of ketones. From the classical work of Ciamician and Silber[2] it is known that if an alcoholic solution of benzophenone is exposed to sunlight, the benzophenone is reduced to benzopinacol at the expense of the alcohol, which is oxidized to aldehyde. Cohen[3] showed that a number of substituted ketones can be reduced to pinacols in the same manner and he found that a variety of primary and secondary alcohols can be used as reducing agents. It appeared that if a small amount of sodium alcoholate was present in the alcoholic solution of the ketone which was exposed to sunlight, a combination of the two reactions would take place: (1) reduction of the ketone to pinacol and (2) decomposition of the pinacol into hydrol and ketone. The ketone that is regenerated in the second reaction would go through the series of reactions until the hydrol was the sole product.

Actually, we found that if a small amount of sodium alcoholate is present in the alcoholic solution, the reduction proceeds exactly as expected; no pinacol is obtained; instead, the hydrol is formed in nearly quantitative yield. For the reaction we employed isopropyl alcohol in preference to ethyl alcohol because the reduction with this alcohol is more rapid and the oxidation product, acetone, is not affected by alkali so readily as is acetaldehyde. The reactions that take place are expressed in the following formulation



$$2(C_6H_5)_2CO + (CH_3)_2CHOH = \begin{array}{c}(C_6H_5)_2C\text{—}OH\\ |\\ (C_6H_5)_2C\text{—}OH\end{array} + (CH_3)_2CO \qquad (1)$$

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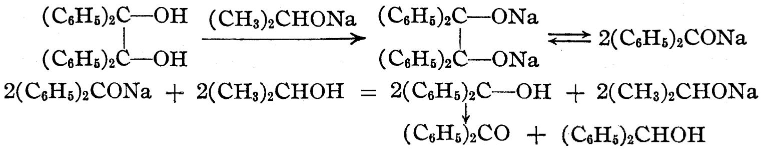
[1] Bachmann, THIS JOURNAL, 55,355 (1933).

[2] Ciamician and Silber, *Ber.*, 33,2911 (1900).

[3] Cohen, *Rec. trav. chim.*, 39,242 (1920).



$$\begin{array}{c}(C_6H_5)_2C{-}OH\\ |\\ (C_6H_5)_2C{-}OH\end{array} \xrightarrow{(CH_3)_2CHONa} \begin{array}{c}(C_6H_5)_2C{-}ONa\\ |\\ (C_6H_5)_2C{-}ONa\end{array} \rightleftharpoons 2(C_6H_5)_2CONa \qquad (2a)$$

$$2(C_6H_5)_2CONa + 2(CH_3)_2CHOH = 2(C_6H_5)_2C{-}OH + 2(CH_3)_2CHONa \qquad (2b)$$

$$\downarrow$$

$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \qquad (2c)$$

As fast as the pinacol is formed by the photochemical reaction (Equation 1) it reacts with the sodium alcoholate and gives sodium pinacolate[4] (Equation 2a). The sodium ketyl radicals[5] produced by dissociation of the sodium pinacolate react with isopropyl alcohol or with pinacol (Equation 2b); one molecule of the ketyl is converted to hydrol as another goes to ketone (2c). The ketone and sodium alcoholate which are regenerated go through the series of reactions until all of the ketone has been converted to hydrol.

In support of this mechanism may be cited the fact that a solution of benzophenone in isopropyl alcohol containing sodium isopropylate becomes greenish-blue on exposure to sunlight, the greenish-blue color being characteristic of the sodium ketyl radical. If the flask containing the colored solution is protected from sunlight, the greenish-blue color disappears, an indication that the reaction represented in Equation 2b is taking place. Renewed exposure to sunlight restores the color. Finally, if this mechanism is correct, then the greenish-blue color should disappear completely when all of the ketone has been reduced. Such is the case. After several days of exposure, the solution becomes colorless and remains so. Indeed, this proved to be a convenient visual indication that the reaction was at an end

Further support for this mechanism was furnished by a comparison of the rate of reduction of benzophenone to benzohydrol with the rate of reduction to benzopinacol. Since the decomposition of the pinacol by sodium alcoholate is very rapid, the rate of reduction to hydrol should be nearly the same as the rate of pinacol formation. Experiment showed that the rates of reduction are practically equal; under nearly identical conditions of exposure, a 93% yield of benzohydrol was obtained when sodium alcoholate was present in the time that a 97% yield of benzopinacol was formed in absence of sodium alcoholate.

Not only benzophenone but a number of other ketones can be reduced to hydrols. In every case the alcoholic solutions of the ketones become colored on exposure to sunlight and this color disappears after several days of exposure. The yields of hydrols varied from 80–95%. Cohen found that Michler's ketone, phenyl α-naphthyl ketone, fluorenone and 4-phenylbenzophenone were not reduced to pinacols on exposing alcoholic solutions of the ketones. In agreement with our view that the pinacols are the

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[4] For an alternate mechanism of the decomposition of pinacol see Ref. 1.

[5] Compare Cohen [*Rec. trav. chim.*, 38, 113 (1919)], who considers that pinacols, or more likely diphenylhydroxymethyl radicals, $(C_6H_5)_2COH$, are intermediate products in the reduction of ketones to hydrols by alkaline reducing agents.

initial products in the reduction to hydrol, it was found that Michler's ketone and phenyl α-naphthyl ketone are not reduced to hydrols; in fact, most of the ketone can be recovered unchanged after prolonged exposure. In like manner, fluorenone is not reduced in the manner of benzophenone; however, the ketone does not remain unaffected but undergoes a reaction which is not a photochemical process. To our surprise 4-phenylbenzophenone was reduced nearly quantitatively to 4-phenylbenzohydrol. According to our mechanism the ketone should give pinacol when an alcoholic solution without sodium alcoholate is exposed. Actually we found that in isopropyl solution the ketone is reduced to the pinacol, 4,4'-diphenylbenzopinacol.

Experimental

Photochemical Reduction of Ketones to **Hydrols.**—Three grams of benzophenone was added to a solution of sodium isopropylate which had been prepared from 0.03 g. of sodium and 30 cc. of anhydrous isopropyl alcohol in a 30-cc. test-tube. The tube was corked and exposed to direct sunlight. Almost immediately the solution assumed a greenish-blue color. This color disappeared when the solution was exposed to air or when it was protected from sunlight. After four days the solution was colorless in bright sunlight, indicating that the reaction was at an end. The solution was poured into an evaporating dish and was diluted with an equal volume of acidified water. On evaporation the benzohydrol crystallized out; it was filtered off, dried and recrystallized from petroleum ether; yield, 2.98 g. (98%). Experiments in which ethyl alcohol was used were not successful because of the reactions undergone by the acetaldehyde.

In one experiment 25 g. of benzophenone in a 150-cc. Pyrex flask was dissolved in 125 cc. of isopropyl alcohol with which 0.25 g. of sodium had reacted. After one week of exposure 20 g. of benzohydrol was obtained. When the reaction was carried out in a long tube the reaction was complete in three days.

A comparison of the rate of reduction to hydrol with the rate of reduction to pinacol was made by exposing two tubes of the same size side by side; one tube contained sodium alcoholate, the other did not. After four days the one tube gave a 93% yield of benzohydrol and the other gave a 97% yield of benzopinacol.

In Table I are given the results obtained by reducing a number of ketones; in each case 3.0 g. of ketone was reduced in the same manner as described for benzophenone. The crude hydrol was recrystallized from a mixture of benzene and petroleum ether; the yields given in the table are based on recrystallized product.

The reaction between fluorenone, isopropyl alcohol and sodium isopropylate is not a photochemical process since the same products result when the mixture is kept in a dark place; heat and not light is the chief factor in hastening the reaction. It is well known that ketones are reduced to hydrols when the ketone is heated for a long time with an alcoholic solution of sodium hydroxide but it is not recognized that the reaction occurs at room temperature with a small amount of sodium alcoholate as it does with fluorenone. We have found that the reaction takes place with benzophenone to a considerable extent under the influence of heat. Five grams of benzophenone was added to a solution of sodium alcoholate prepared from 0.06 g. (10%) of sodium and 20 cc. of isopropyl alcohol and the mixture was refluxed for fifteen hours on a steam-bath; hydrolysis gave 3.92 g. (78%) of benzohydrol. The reaction is best explained by the following formulation which shows that a small amount of sodium alcoholate should be sufficient for reduction

$$(C_6H_5)_2CO + (CH_3)_2CHONa \longrightarrow (C_6H_5)_2CHONa + (CH_3)_2CO \qquad (3)$$

$$(C_6H_5)_2CHONa + (CH_3)_2CHOH \rightleftharpoons (C_6H_5)_2CHOH + (CH_3)_2CHONa \qquad (4)$$

TABLE I

PHOTOCHEMICAL REDUCTION OF KETONES TO HYDROLS

Ketone	Color during reduction	Time of exposure, days	Hydrol yield, %
Benzophenone	Greenish-blue	4	98
4-Methylbenzophenone	Greenish-blue	6	95
4,4'-Dimethylbenzophenone	Blue	6	90
4-Methoxybenzophenone	Greenish-blue	6	90
4-Chloro-4'-methylbenzophenone[a]	Blue	7	80
4-Phenylbenzophenone[b]	Green	7	95
4-Chlorobenzophenone	Green	7	80
Michler's ketone[c]	None	33	00
Phenyl α-naphthyl ketone[d]	None	15	00
Fluorenone[e]	......	7	

[a] The yields of halogen-substituted hydrols are lower because some of the halogen is removed in the reaction. This is especially true when the halogen is in the ortho position; the corresponding hydrols cannot be prepared conveniently by this method.

[b] Although Cohen reported that this ketone is not reduced to the pinacol in ethyl alcohol solution, we find that the reduction took place when a suspension of the ketone in isopropyl alcohol was exposed to sunlight. The pinacol was recrystallized from a mixture of acetone and chloroform and was obtained in the form of colorless needles which melted at 198° and which proved to be identical with the pinacol produced by reduction of the ketone by a mixture of magnesium and magnesium iodide [Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927)].

[c] After thirty-three days of exposure, 80% of the ketone was recovered; some decomposition products were present.

[d] A 70% yield of pure ketone was recovered.

[e] Three tubes containing isopropyl alcohol solutions of fluorenone were exposed simultaneously. One tube contained no sodium alcoholate; another tube had sodium alcoholate in it; the third tube contained sodium alcoholate but the tube was wrapped in a black cloth. The tube that contained no sodium alcoholate remained unchanged; after twenty-two days of exposure the fluorenone was recovered entirely unaffected. Both tubes containing sodium alcoholate became dark-brown and nearly black in color; after six days the solution was light-brown. Hydrolysis gave a 44% yield of fluorenol from the uncovered tube and a 56% yield from the covered tube. Prolonged exposure gave fluorenone and other products. Practically the same results were obtained from a solution which was kept in the dark for the same length of time.

A study is being made of the action of this reducing mixture on other ketones and on other types of compounds. In order to determine whether any benzohydrol is formed by this reaction by the heat received during exposure to sunlight, two tubes were exposed side by side, one of which was wrapped in a black cloth. In the time that the uncovered tube gave a 93% yield of benzohydrol, only 10% of the ketone in the covered tube was affected. The products presented in Table I represent, therefore, the results of photochemical reduction nearly entirely.

Preparation of Benzopinacol by Photochemical Reduction of Benzophenone.—We have confirmed the excellent work of Cohen,[6] who obtained a quantitative yield of benzopinacol by exposing 10 g. of benzophenone in 16 cc. of isopropyl alcohol. From the standpoint of preparation we find it more convenient to use a larger amount of alcohol and have prepared benzopinacol by the procedure which follows. A solution of 50 g. of

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[6] Cohen, Rec. trav. *chim.*, 39, 245 (1920).

benzophenone in 450 cc. of isopropyl alcohol contained in a 500-cc. round-bottomed Pyrex flask is supported in an inverted position on a tripod and exposed to direct sunlight. After three hours crystals of benzopinacol are present. After one week 45 g. of benzopinacol is filtered off. To the filtrate is added a further 50 g. of ketone and the solution is again exposed to sunlight. This procedure was repeated until 300 g. of pinacol was obtained.

In one experiment a solution of 400 g. of benzophenone in 400 cc. of isopropyl alcohol and 400 cc. of benzene was exposed. After one month a quantitative yield of pinacol was obtained. The disadvantage of using benzene lies in the fact that the pinacol crystallizes with benzene of crystallization in the form of a compact mass which is difficult to remove from the flask.

Summary

Benzophenone and certain substituted benzophenones are reduced nearly quantitatively to hydrols when solutions of the ketones and a small amount of sodium isopropylate in isopropyl alcohol are exposed to sunlight.

The mechanism of the reaction has been elucidated. The ketone is reduced initially to the corresponding pinacol by a photochemical reaction; the pinacol is then converted to a mixture of ketone and hydrol by the action of the sodium alcoholate and alcohol; the ketone that is regenerated in this manner goes through the series of reactions again.

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Researches on Nitrogenous Glycosides. II. The Synthesis of Glycosido Ureides[1]

BY KATHERINE M. HARING AND TREAT B. JOHNSON

The present investigation[2] was undertaken in order to develop a general method for the preparation of glycosido ureides of the hydantoic acid and hydantoin types. Glycosidohydantoins and their reduced forms, the unknown glycosidoimidazoles, are of interest because of their structural relationship to the natural purine nucleosides. In addition, it was believed that a study of such nitrogenous glycosides would be of biochemical importance in relation to the problem of the structure of naturally occurring protein-carbohydrate complexes.

The interest in the latter field has recently received an added stimulus in the discovery that carbohydrate units form integral parts of the proteins of blood serum[3] and egg white,[4] which were formerly considered simple

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(1) Constructed from a dissertation presented by Katherine M. Haring to the Faculty of the Graduate School of Yale University in June, 1932, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) The research described was supported in part by a grant from the Therapeutic Research Committee of the American Medical Association for 1930–1931 and 1931–1932.

(3) Rimington, *Biochem. J.*, 23, 430 (1929); 25, 1062 (1931).

(4) Levene and Mori, *J. Biol. Chem.*, 84, 49 (1929).

proteins. Furthermore, since bacterial polysaccharides which in the free state show typical hapten reactions, exist in the bacteria in a state which renders them not only type specific but also antigenic, it is believed that they must be joined to another molecule—probably protein. The most striking evidence in favor of this view has been contributed by the researches of Goebel and Avery.[5]

Since carbohydrate fractions appear to be intimate parts of the structure of certain simple proteins and since there is evidence that bacterial polysaccharides may be associated with proteins in the parent cell, it becomes very important to study the kinds of linkages which might exist between them. The carbohydrates of serum proteins and of egg proteins have been found to be very firmly bound in the combined molecules, whereas several bacterial polysaccharides have easily been obtained in the free state. It is probable, therefore, that the types of linkages involved in such cases vary widely.

The method of coupling sugars with amino acids by direct union with the free amino groups gives combinations which are easily susceptible to hydrolysis. A synthetic compound resulting from such a union was obtained by Euler and Zeile,[6] who condensed glycine ester with glucose in the presence of active aluminum. Maurer and his co-workers[7] had previously studied the reaction between bromoacetoglucose and sarcosine amide. They were able to deacetylate the resulting compound to obtain sarcosine amide glycoside. An extension of this method to other amino acids and peptides led to the formation of a number of acetylated derivatives. Euler was able to apply Maurer's method further to the preparation of glycylglycine glycoside. Both Maurer and Euler found that these derivatives which contained glucose directly linked to the amino acids or peptides were unstable in aqueous alkali solution.

The main object of the research presented here has been to develop a general method for coupling amino acids with sugars through an urea bridge. The synthetic methods which are involved in the preparation of glycosidothiohydantoic acid (VII), N-1-glycosido-2-thiohydantoin (VI), glycosidohydantoic acid (VIII), and N-1-glycosidohydantoin (IX) are shown in the accompanying chart.

Tetracetylglucose isothiocyanate, which was described originally by Fischer,[8] condensed smoothly and almost quantitatively with glycine ethyl ester hydrochloride, in the presence of pyridine, to give ethyl tetracetyl glycosidothiohydantoate (I). The practically quantitative removal of the acetyl groups from (I) with the formation of ethyl glycosidothiohydantoate (III) was accomplished by the use of alcoholic hydrogen chloride. It was

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(5) Goebel and Avery, J. *Exp. Med.*, *64*, 431, 487 (1931).

(6) Euler and Zeile, Ann., 487, 163 (1931).

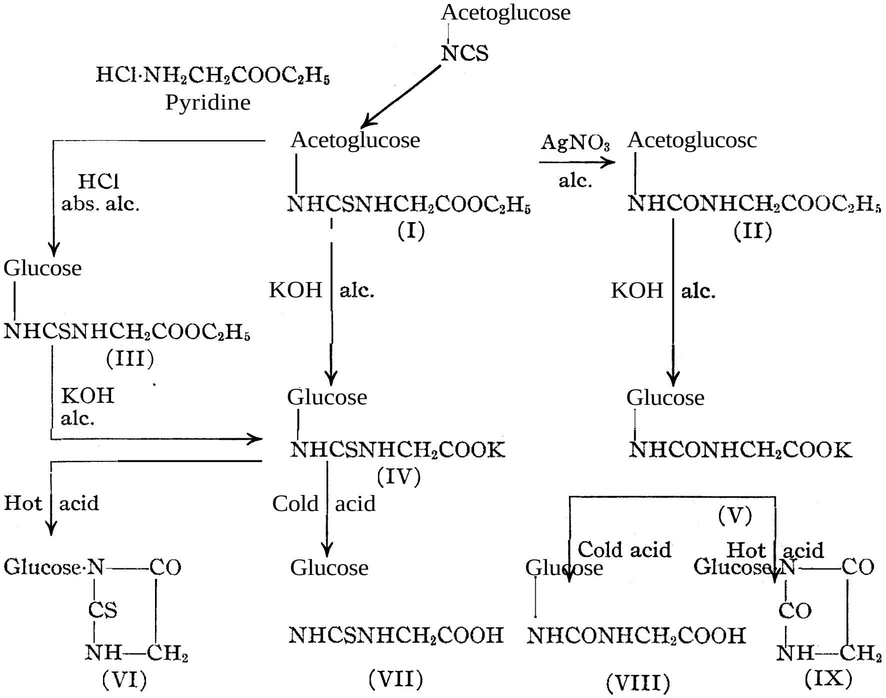
(7) Maurer and Schiedt, Z. *physiol. Chem.*, *206*, 125 (1932).

(8) Fischer, *Ber.*, 47, 1382 (1914).

more practical, however, to simultaneously deacetylate and deesterify (I) by saponification with alcoholic potassium hydroxide. The potassium salt (IV) which resulted could be subsequently hydrolyzed with cold acid to give glycosidothiohydantoic acid (VII) or with hot acid to give N-1-glycosido-2-thiohydantoin (VI).

The oxygen analogs of the compounds which have been described were prepared from ethyl tetracetylglycosidohydantoate (II). This substance resulted when ethyl tetracetylglycosidothiohydantoate (I) was treated with alcoholic silver nitrate solution according to the procedure described by Dixon[9] for the desulfurization of thioureas. Deacetylation and deesterification of (II) was accomplished by saponification with alcoholic potassium hydroxide. The resulting potassium salt (V) was then transformed with cold acid into glycosidohydantoicacid (VIII) or with hot acid into N-1-glycosidohydantoin (IX).

SYNTHESIS OF GLYCOSIDO UREIDES



The glycosido ureides prepared in this investigation resemble the glycosido amino acid and peptide combinations of Euler and Zeile and Maurer and Schiedt in their behavior toward hydrolytic agents. On the other hand, they show a marked contrast to the purine and pyrimidine glycosides described in the literature. The purine nucleosides are readily hydrolyz-

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(9) Dixon, *J. Chem. Soc.*, 556 (1895).

able by acids but remain intact on treatment with alkalies, whereas the pyrimidine nucleosides are much more resistant even to acid hydrolysis.[10] Glycosidohydantoic acid (VIII) and N-1-glycosidohydantoin (IX), however, represent a type of glycoside which is much more susceptible to hydrolysis than the purine nucleosides since they readily reduce Fehling's solution. In the case of glycosidothiohydantoic acid (VII) and N-1-glycosido-2-thiohydantoin (VI) colored side reactions make it impossible to observe any reduction with Fehling's solution although hydrolysis probably does occur. The ease with which these compounds are hydrolyzed by hot acid has been shown to be one of the factors which causes the small yields in the preparation of both N-1-glycosido-2-thiohydantoin and N-1-glycosidohydantoin. Research will be continued in this field in order to extend the method of synthesis, which has been described, to other sugars and to other amino acids and peptides.

Experimental Part

Tetracetyl-*d*-glucose Isothiocyanate.—For the preparation of tetracetylglucose isothiocyanate a modification of Fischer's method[8] was found necessary.

A solution of 25 g. of bromoacetoglucose in 150 cc. of xylene was treated with 16 g. of solid silver thiocyanate. The mixture was refluxed over a small free flame for one to two hours until the supernatant liquid became reddish-brown. The solution was then allowed to cool, filtered from the silver salts, and diluted with about 100 cc. of petroleum ether. The red-brown gum which in most cases was thrown out on the stirring rod and sides of the beaker was discarded. Tetracetylglucose isothiocyanate was precipitated by slowly decanting the supernatant liquid from the red gum into 250 cc. of iced petroleum ether. The total yield varied from 50–87%.

The crude isothiocyanate could be recrystallized from a hot alcohol solution which was cooled quickly in an ice-bath or from a chloroform solution which was poured slowly into a large volume of petroleum ether. The latter method was more satisfactory. The products from the two methods of recrystallization did not show the different characteristics which Fischer described. In either case the purified compound melted at 112–114°.[11]

Ethyl Tetracetyl-d-glycosidothiohydantoate (I).—Eight grams of glycine ethyl ester hydrochloride was suspended in a solution of 20 g. of tetracetylglucose isothiocyanate and 6 cc. of pyridine in 150 cc. of chloroform and the mixture was refluxed on the steam-bath for at least three hours. When heating was discontinued the chloroform solution was evaporated to dryness *in oacuo*. The residual gum was stirred vigorously with 100–150 cc. of water and was alternately warmed on the steam-bath and cooled in ice until it hardened. Incomplete removal of the chloroform occasionally prevented the hardening of the gum. After standing in the ice-bath the caked product could be crushed to a powder. The yield was 96%.

Ethyl tetracetylglucosidothiohydantoate was very soluble in acetone and hot ethyl alcohol, soluble in cold ethyl alcohol (1 g. in 20 cc.), cold methyl alcohol, and cold benzene, and practically insoluble in ether, petroleum ether and water. Twenty-two grams of crude material was recrystallized from about 300 cc. of 50% alcohol. The purified substance separated in rosets of short, creamy-white needles which melted at 151–152.5°. Its specific rotation was $[\alpha]^{22}_{D}$ +6° in chloroform solution. A sample was dried *in vacuo* at 100° for analysis.

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(10) Levene and Bass, "Nucleic Acids," Chemical Catalog Co., New York, 1931, pp. 144–145.

(11) The melting points given are corrected melting points.

Anal. Calcd. for $C_{19}H_{28}O_{11}N_2S$: C, 46.34; H, 5.72; N, 5.69; S, 6.50. Found: C, 46.43; H, 5.68; N, 5.68; S, 6.50.

If the time of heating the original reaction mixture was less than three hours, small amounts of tetracetylglucose thiourethan, melting at 156–157°, were isolated from the recrystallization filtrate, showing that the reaction had been incomplete. Mixed with tetracetylglycosidothiohydantoic ester, this compound melted at 129–131°.

Ethyl d-Glycosidothiohydantoate (III).—Ethyl tetracetylglycosidothinhydantoate (1) could be deacetylated either in acid or alkaline medium. When alcoholic hydrogen chloride was the reagent used, the product was ethyl glycosidothiohydantoate.

Five cc. of absolute alcohol saturated with dry hydrogen chloride was added to a warm solution of 10 g. of ethyl tetracetylglycosidothiohydantoate in 100 cc. of absolute alcohol. After this solution had stood overnight at room temperature it was concentrated to a thick sirup, diluted with absolute alcohol and concentrated again. It was then diluted once more with 100 cc. of absolute alcohol and again allowed to stand in the ice box. The total yield of ester obtained by carrying out this procedure repeatedly was 95%.

Ethyl glycosidothiohydantoate crystallized in iridescent, white plates which contained alcohol of crystallization. It was very soluble in water, soluble in hot absolute alcohol (1 g. in 50 cc.) and hot ethyl acetate (1 g. in 230 cc.), but much less soluble in cold absolute alcohol (1 g. in 400 cc.) and cold ethyl acetate (1 g. in 1100 cc.). It could be recrystallized from either of the latter solvents. The melting point of the purified product was indistinct. It softened at about 110" and melted with the evolution of gas at 119–121°. If the heating was more rapid it melted only partially with the evolution of gas at 119–121° and liquefied completely at 154–155°. Its optical rotation was $[\alpha]^{22}_{D}$ −31.3" in water solution. A sample, dried to constant weight *in vacuo* at room temperature, gave analyses showing the presence of one mole of alcohol of crystallization.

Anal. Calcd. for $C_{11}H_{20}O_7N_2S \cdot C_2H_5OH$: N, 7.57. Found: N, 7.52, 7.44.

This crystalline form of the product could be freed from alcohol only with great difficulty due to its tendency to decompose on prolonged heating. The best result was obtained when a sample was heated in an Abderhalden drier over calcium chloride at 76° for six weeks and then at 100° for two days. The total loss in weight was 12.97%. This corresponded to the theoretical loss in weight of 12.44% due to one mole of alcohol of crystallization. The alcohol-free product was a tan colored powder which melted at 152–155° and decomposed at about 162°.

Anal. Calcd. for $C_{11}H_{20}O_7N_2S$: N, 8.64. Found: N, 8.69.

When this alcohol-free modification was recrystallized from absolute alcohol it reverted to the original crystalline form.

When a large excess of alcoholic hydrogen chloride was used to catalyze the deacetylation of (I), the monohydrochloride of ethyl glycosidothiohydantoate was formed as a by-product. It was precipitated by pouring dropwise into a large volume of dry ether the sirupy alcoholic filtrate from which ethyl glycosidothiohydantoate itself had been separated. Purification of the hydrochloride could be accomplished by dissolving it in absolute alcohol and reprecipitating it with dry ether. The purified substance was a tan, amorphous powder which was very hygroscopic. When dry it melted with the evolution of gas at 73–75°.

Anal. Calcd. for $C_{11}H_{20}O_7N_2S \cdot HCl$: N, 7.76; HCl, 10.11. Found: N, 7.58, 7.50: HCl, 10.25.

Potassium d-Glycosidothiohydantoate (IV).—When alcoholic potassium hydroxide was the reagent used to deacetylate (I), the ester grouping was saponified simultaneously and potassium glycosidothiohydantoate was formed. Alcoholic potassium hydroxide was used in preference to alcoholic ammonia because the potassium salt which resulted was more satisfactory to handle than the corresponding ammonium salt.

A solution of 1.5 g. of potassium hydroxide in 20 cc. of alcohol was added to a warm solution of 5 g. of ethyl tetracetylglycosidothiohydantoate in 75 cc. of alcohol. A flocculent pink precipitate was formed immediately when the two solutions were mixed. When the supernatant liquid had become clear the pink solid was filtered and washed with alcohol. When dry it was a hygroscopic, pink powder which decomposed at 137–141°. It could be prepared equally well by the saponification of (III) with alcoholic potash. Potassium glycosidothiohydantoate was used in the crude state for the preparation of glycosidothiohydantoic acid (VII) and N-1-glycosido-2-thiohydantoin (VI).

***d*-Glycosidothiohydantoic Acid (VII).**—A water solution of 5 g. of potassium glycosidothiohydantoate was treated with 4 cc. of approximately 6 *N* sulfuric acid and the mixture was allowed to stand for four hours at room temperature. It was then concentrated *in vacuo* and poured into about 200 cc. of absolute alcohol. The filtrate from the precipitated potassium sulfate was concentrated again *in vacuo* until crystals of glycosidothiohydantoic acid separated. The maximum yield was 54%. If a considerable excess of sulfuric acid was used originally to neutralize the potassium salt, the mother liquor yielded finally crystals of ethyl glycosidothiohydantoate which evidently resulted from the esterification of the free acid.

The crude acid was recrystallized from alcohol. One gram dissolved very slowly in about 300 cc. of boiling alcohol. Since the solubility of the acid was not appreciably greater in hot than in cold alcohol, the solution was concentrated to half volume or less before cooling. The recrystallized compound decomposed at 180.5-181" when it was heated slowly. Rapid heating raised the decomposition point several degrees. Its specific rotation was $[\alpha]^{22}_{\rm D}$ −36.1° in water solution. A sample was dried at 100° *in vacuo* for analysis.

Anal. Calcd. for $C_9H_{16}O_7N_2S$: C, 36.49; H, 5.45; N, 9.46. Found: C, 36.45; H, 5.50; N, 9.46, 9.39.

When a water solution of (VII) was boiled with Fehling's solution it became dark gray-green. The precipitate which settled was dark brown. Probably the sulfur caused side reactions which made it impossible to observe the reduction.

N-1-*d*-Glycosido-2-thiohydantoin (VI).—N-1-Glycosido-2-thiohydantoin was prepared by heating a solution of 2 g. of potassium glycosidothiohydantoate in 50 cc. of approximately 6 *N* hydrochloric acid for one-half hour on the steam-bath. The solution was then concentrated *in vacuo* to about 10 cc. and poured into 50 cc. of absolute alcohol. The precipitate of potassium chloride which formed was filtered out and the filtrate was concentrated *in vacuo* to a thin sirup which was diluted with about 50 cc. of amyl alcohol. The cloudy solution which resulted was concentrated *in vacuo* until an amorphous precipitate began to form on the sides of the flask. This product, which shriveled at about 70° and decomposed at 111–121°, was discarded. The filtrate, when concentrated further *in vacuo*, yielded fine, yellow crystals of glycosidothiohydantoin, which decomposed at about 226°. The maximum yield was 33%.

This compound was recrystallized from absolute alcohol. One gram dissolved slowly in about 85 cc. of boiling alcohol and was about one-half as soluble cold. The purified product separated in the form of pale yellow plates which darkened when heated at about 216° and melted with decomposition at 224225". Its specific rotation was $[\alpha]^{22}_{\rm D}$ +22.8° in water solution. A sample was dried at 100° *in vacuo* for analysis.

Anal. Calcd. for $C_9H_{14}O_6N_2S$: C, 38.86; H, 5.08; N, 10.07. Found: C, 39.22; H, 5.17; N, 9.87.

When a water solution of N-1-glycosido-2-thiohydantoin was added to Fehling's solution it turned yellowish-brown in the cold and formed a dark yellow precipitate on heating. Since N-1-glycosidohydantoin reduced Fehling's solution under similar conditions, it is probable that the sulfur in the former case caused the colored side reactions.

In addition to glycosidothiohydantoin, the amyl alcohol mother liquor from the reaction previously described yielded a second type of crystalline compound. When heated, it turned dark brown at about 199° and decomposed at 221–231°. It could be recrystallized from absolute alcohol but was more soluble in amyl alcohol than glycosidothiohydantoin and much less soluble in water. Nitrogen analyses did not serve to identify the substance as thiohydantoic acid or thiohydantoin but indicated clearly that the glucose part of the molecule was no longer present. The latter conclusion was supported further by the fact that this was the only crystalline product which resulted when the original reaction mixture was heated for periods longer than one-half hour. N-1-Glycosido-2-thiohydantoin was apparently not very stable toward acid hydrolysis.

Ethyl Tetracetyl-*d*-glycosidohydantoate (II).—Ethyl tetracetylglycosidohydantoate was prepared by desulfurizing (I).

A hot solution of 10 g. of ethyl tetracetylglycosidothiohydantoate in 150 cc. of alcohol and a solution of 7.5 g. of silver nitrate in 20 cc. of water were mixed and heated on the steam-bath. After five minutes an alcoholic solution of 2.2 g. of potassium hydroxide was added to neutralize the nitric acid set free from the silver nitrate. This promoted the coagulation of the silver sulfide and helped to prevent the nitric acid from hydrolyzing off the acetyl groups of the sugar. The solution was heated until the silver sulfide coagulated. Then it was cooled and filtered through a norit mat. The filtrate was concentrated *in vacuo* to about 50 cc. and diluted with 3-4 volumes of water. When the solution was stirred vigorously to start precipitation the desulfurized ester was obtained in 48% yield.

Ethyl tetracetylglycosidohydantoate was recrystallized from absolute alcohol. One gram was soluble in about 10 cc. of hot and about 30 cc. of cold absolute alcohol. It was practically insoluble in water but was much more soluble in 50% than in absolute alcohol. The recrystallized product separated in the form of long, white needles which melted at 149–149.5°. Its specific rotation was $[\alpha]_D^{22}$ $-3°$ in chloroform solution. A sample was dried at 100° *in vacuo* and analyzed.

Anal. Calcd. for $C_{19}H_{28}O_{12}N_2$: C, 47.89; H, 5.92; N, 5.88. Found: C, 47.57; H, 5.93; N, 5.93.

Potassium d-Glycosidohydantoate (V).—A solution of 1.5 g. of potassium hydroxide was added to a warm solution of 5 g. of ethyl tetracetylglycosidohydantoate in 75 cc. of alcohol. A white precipitate of potassium glycosidohydantoate formed immediately. The crude salt, which decomposed at 134–137°, was used in the preparation of glycosidohydantoic acid (VIII) and N-1-glycosidohydantoin (IX).

d-Glycosidohydantoic Acid (VIII).—Twenty cc. of approximately 1 *N* hydrochloric acid was added to a water solution of 4 g. of potassium glycosidohydantoate and the mixture was allowed to stand at room temperature. After four hours the solution was concentrated *in vacuo* to about *10* cc. and diluted with 100 cc. of absolute alcohol. When the filtrate from the precipitated potassium chloride was allowed to stand in the ice-bath crystals of glycosidohydantoic acid separated. The total yield was 55%.

The crude product was recrystallized from alcohol. One gram dissolved in 80 cc. of boiling and in 500 cc. of cold alcohol. The purified acid readily reduced Fehling's solution. It melted with decomposition at 169.5–170° when it was heated slowly and had a specific rotation of $[\alpha]_D^{27}$ $-25.8°$ in water solution. A sample was dried at 100° *in vacuo* and analyzed.

Anal. Calcd. for $C_9H_{16}O_8N_2$: C, 38.57; H, 5.71; N, 10.00. Found: C, 38.40; H, 5.95; N, 9.82, 9.90.

N-1-*d*-Glycosidohydantoin (IX).– A solution of 2 g. of potassium glycosidohydantoate in 25 cc. of approximately 6 *N* hydrochloric acid was heated on the steam-bath for one-half hour. It was then concentrated *in vacuo* to about 10 cc. and poured into 100 cc. of absolute alcohol. The filtrate from the precipitated potassium chloride was concentrated *in vacuo,* diluted with more absolute alcohol and concentrated again to about 25 cc. This thin sirup was diluted with about 75 cc. of amyl alcohol, cooled in an ice-bath and filtered from the sticky, amorphous precipitate which formed. This product, which shriveled at 60° and decomposed at 110–115°, was discarded. When the mother liquor was cooled further in the ice-bath fine, white crystals of N-1-glycosidohydantoin were deposited on the walls of the beaker. The total yield was 25%.

The crude product was very slightly soluble in hot absolute or 95% alcohol. It could best be recrystallized by dissolving it in cold 50% alcohol, adding 3–4 volumes of absolute alcohol and concentrating the resulting solution until crystals just began to separate. When the concentrated solution was allowed to stand in the ice box, N-1-glycosidohydantoin crystallized in rosets of very short, fine, white needles, which decomposed at 270–271°. Its specific rotation was $[\alpha]^{22}_{D}$ +5° in water solution. When it was boiled with Fehling's solution there was a decided reducing effect. A sample was dried *in vacuo* at 100° and analyzed.

Anal. Calcd. for $C_9H_{14}O_7N_2$: C, 41.22; H, 5.39; N, 10.69. Found: C, 40.98; H, 5.46; N, 10.63.

The amyl alcohol mother liquor yielded, in addition to N-1-glycosidohydantoin, small amounts of a second crystalline compound which melted with decomposition at about 178–194°. Further work will be necessary to identify it. Probably, however, as in the case of the second compound isolated from the preparation of N-1-glycosido-2-thiohydantoin, this compound had also lost the glucose part of the molecule.

Summary

1. A general method has been developed for the synthesis of four new glycosido ureides, d-glycosidothiohydantoic acid (VII), N-1-*d*-glycosido-2-thiohydantoin (VI), d-glycosidohydantoic acid (VIII), and N-1-*d*-glycosidohydantoin (IX). This investigation involved the preparation of a number of intermediate acetylated and deacetylated derivatives of glycosidothiohydantoic acid and glycosidohydantoic acid.

2. A study of the final glycosido ureides has shown that they differ in chemical properties from the synthetic glycosido pyrimidines and purines, but resemble the synthetic glycosido amino acids and peptides which have been described in the literature.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Orientation in the Furan Nucleus. III. 5-Methyl-3-furoic Acid[1]

BY HENRY GILMAN, ROBERT R. BURTNER AND E. W. SMITH

Introduction

It is rather astonishing that despite the long history of furan compounds very little is known definitely concerning orientation in the furan nucleus. There are several reasons for this. First, furan compounds are reputedly highly sensitive to acidic reagents, and it is just such reagents which are most commonly involved in substitution reactions such as halogenation, nitration and sulfonation. Second, there is a pronounced tendency for substituents to occupy the alpha-positions when these are available. This makes the determination of the position of substituents in furan more difficult than in benzene, for absolute methods of orientation (like those used with signal success in the classical studies by Korner with benzene) are of limited application because not all of the theoretically possible isomers are formed in a given substitution reaction starting with furan or a mono-substituted furan or a di-substituted furan. Furthermore, if all possible isomers were formed and could be isolated, the absolute method for orientation would be of restricted applicability as can be readily ascertained by a comparison of isomeric furan and benzene types. Third, it is, at present, difficult to obtain beta-substituted furans, even by indirect methods, and only very recently have the simple beta-substituted furans like 3-furaldehyde, 3-furansulfonic acid, 3-chloromercurifuran, etc., become accessible. Fourth, analogies cannot be made confidently with related heterocycles like thiophene. Not only are there essential differences between thiophene and furan, but (and this is of greater importance) the positions of elements and groups in many nuclear substituted thiophenes have not been determined unequivocally. Furthermore, it appears that the structures now assigned to some nuclear substituted thiophenes are incorrect, and it would not be very surprising to find that analogies, if any are to be drawn, will be with furan and not with thiophene as a type. Fifth, physico-chemical methods have a particularly circumscribed utility, at this time, for such methods in general turn on comparisons with compounds of known constitution as standards, and relatively few such compounds are available.

The particular need is for reference or standard compounds having two nuclear substituents. Theoretically, there are four isomeric di-substituted furans, in which the nuclear substituents are alike. The paucity of reference compounds becomes obvious when we learn that there is no single, complete series of di-substituted furans having two like substituents.

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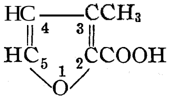
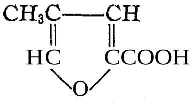
(1) For preceding papers in this series see: Gilman and Wright, *Iowa State Coll. J. Sci.*, **5**, 85 (1931); Gilman, Burtner and Smith, *Rec. trav. chim.*, **51**, 407 (1932).

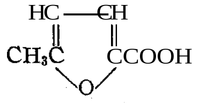
Theoretically, there are six isomeric di-substituted furans, in which the nuclear substituents are unlike. The present synthesis of 5-methyl-3-furoic acid (Formula VI) completes such a series, and makes available for the first time a group of reference compounds for the determination of the position of substituents in poly-substituted furans having both like and unlike substituents.



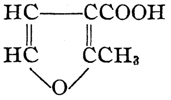
m. p. 134°
(I)[2]



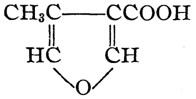
m. p. 129°
(II)[3]



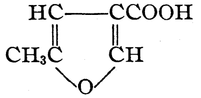
m. p. 109°
(III)[4]



m. p. 101°
(IV)[5]



m. p. 138–139°
(V)[6]



m. p. 119°
(VI)

The 5-methyl-3-furoic acid (VI) was synthesized by the following sequence of reactions

$$3,5\text{-}C_4H_2O(COOH)_2 \longrightarrow 3,5\text{-}C_4H_2O(COOCH_3)_2 \longrightarrow$$
$$3,5\text{-}C_4H_2O(COOCH_3)(COOH) \longrightarrow 3,5\text{-}C_4H_2O(COOCH_3)(COCl) \longrightarrow$$
$$3,5\text{-}C_4H_2O(COOCH_3)(CHO) \longrightarrow 3,5\text{-}C_4H_2O(COOH)(CHO) \longrightarrow$$
$$3,5\text{-}C_4H_2O(COOH)(CH{=}NNH_2) \longrightarrow 3,5\text{-}C_4H_2O(COOH)(CH_3).$$

The constitution of 5-methyl-3-furoic acid was confirmed by other reactions. First, it is known that one of the carboxyl groups in the initial dibasic acid occupies a 8-position, because preferential pyrolytic decarboxylation gives 3-furoic acid. Second, the methyl group in the ultimate product (a methyl-3-furoic acid) is in an a-position because decarboxylation yields 2-methylfuran (or sylvan). Only two α-methyl-β-furoic acids are possible: namely, IV and VI, and the new methylfuroic acid is certainly quite unlike the well-known 2-methyl-3-furoic acid (IV).

Experimental Part

Dimethyl 2,4-furandicarboxylate was obtained in a 90% yield in accordance with the directions of Feist.[7]

4-Carbomethoxy-2-furoic Acid, $C_4H_2O(COOCH_3)(COOH)$.—One-tenth mole of potassium hydroxide in 50 cc. of absolute methyl alcohol was added to 0.1 mole of the dimethyl ester in 50 cc. of methyl alcohol, and after refluxing until no color test was observed with phenolphthalein, the ester salt was acidified in the cold with hydrochloric acid to yield 14.5 g. of the ester acid melting at 100–105°. Crystallization from water

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(2) Asahina, *Ada Phytochimica*, 2, 1 (1924).

(3) Rinkes, *Rec. trav. chim.*, 50, 1127 (1931).

(4) Hill, *Ber.*, 22, 607 (1889); Blanksma, *Chem. Weekblad*, 33, 33 (1912).

(5) Plancher and Albini, *Atti. acad. Lincei*, [5] **13**, *I*, 39 (1904); Benary, *Ber.*, **44**, 493 (1911); Gilman, Burtner and Smith, *Rec. trav. chim.*, *51*, 407 (1932).

(6) Reichstein and Zschokke. *Helv. Chim. Acta*, **14**, 1270 (1931).

(7) Feist, *Ber.*, 34, 1992 (1901).

yielded lustrous white plates melting at 132.5°; neutralization equivalent, calcd., 170; found, 172.8.

Anal. Calcd. for $C_7H_6O_5$: C, 49.41; H, 3.56. Found: C, 49.42; H, 3.85.

4-Carbomethoxy-2-furoyl Chloride, $C_4H_2O(COOCH_3)(COCl)$.—The ester acid chloride was prepared by heating (after the initial vigorous reaction) a benzene solution of the ester-acid with thionyl chloride; and, on recrystallization from carbon tetrachloride. it melted at 83–84"

Anal. Calcd. for $C_7H_5O_4Cl$: Cl, 18.81. Found: Cl, 18.86 and 18.63.

4-Carbomethoxy-2-furaldehyde, $C_4H_2O(COOCH_3)(CHO)$.—Catalytic reduction was effected by the procedure of Rosenmund.[8] A few details will be given because the method has not been described for furan compounds and we have had consistent success in converting a miscellany of furoyl chlorides to the corresponding furaldehydes. Four and one-half grams (0.023 mole) of the ester acid chloride, 1.8 g. of the palladium–barium sulfate catalyst and 25 cc. of dry xylene were placed in a 200-cc. three-necked flask provided with a stirrer, condenser and delivery tube for admitting hydrogen. A small U-tube containing sulfuric acid was attached to the end of the condenser to prevent the entry of moisture and to serve as an indicator for the pressure of hydrogen. The mixture was gently refluxed (bath temp., 125°) with vigorous stirring, and a stream of dry hydrogen was bubbled through at a rate to maintain a slight positive pressure. Hydrogen chloride was evolved immediately, and reduction was continued until no further hydrogen chloride was evolved. The cooled mixture was filtered, and after removing the solvent there remained 3.5 g. of a pale yellow solid melting at 91–92°. After crystallization from methyl alcohol the ester aldehyde melted at 93.5°. The yield was 99%, and the compound gave positive Schiff and aniline acetate tests. The phenylhydrazone of 4-carbomethoxy-2-furaldehyde is a tan crystalline compound melting at 114–115°.

Anal. Calcd. for $C_7H_6O_4$: C, 54.54; H, 3.89. Found: C, 54.68; H, 3.62.

4-Carboxy-2-furaldehyde, $C_4H_2O(COOH)(CHO)$.—Hydrolysis of the ester aldehyde, by refluxing 3.5 g. with 50 cc. of 6 N hydrochloric acid for fifteen minutes, gave a 94% yield of the acid aldehyde which, after crystallization from hot water, melted at 158–159°. This compound also gave the above-mentioned aldehyde tests; neutralization equivalent, calcd., 140; found, 143.1.

4-Carboxy-2-furaldehyde Hydrazone, $C_4H_2O(COOH)(CH{=}NNH_2)$.—A 90% yield of the hydrazone, melting at 145–146°, was obtained from 2.9 g. of the acid aldehyde and 2.1 g. of hydrazine hydrate in 10 cc. of absolute ethyl alcohol. The mixture, kept initially at about −15° for one and one-half hours, was warmed for a few minutes at about 75° and then worked up in a customary manner.

5-Methyl-3-furoic Acid, $C_4H_2O(COOH)(CH_3)$.—The hydrazone was converted by the usual Wolff–Kischner method to the methylfuroic acid by means of potassium hydroxide (pellets) and absolute ethyl alcohol. A slight evolution of gas was noticed during a two-hour period of heating at about 70°, and after standing overnight at room temperature, heating was continued for four hours, at the end of which time gas evolution had practically ceased. The yield of 5-methyl-3-furoic acid was 31%, and the compound melts at 119° after crystallization from hot water; neutralization equivalent, calcd., 126; found, 130.

Anal. Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.76. Found: C, 56.91; H, 5.32.

Decarboxylation to 2-Methylfuran, $C_4H_3OCH_3$.—Decarboxylation of 0.9 g. of 5-methyl-3-furoic acid by the method of Johnson using quinoline and copper–bronze was effected at 215'. The evolution of carbon dioxide commenced at about 200°, and the

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(8) Rosenmund and Zetzsche, *Ber.*, 51, 578 (1918).

reaction product when worked up in a customary manner gave about 0.5 cc. of a clear. pleasant smelling liquid. This was definitely identified as 2-methylfuran by converting it to 5-methyl-2-chloromercurifuran by means of mercuric chloride and sodium acetate. A mixed melting point determination with an authentic specimen melting at 132° showed no depression.

Summary

The first complete series of di-substituted furans, particularly useful as reference or standard compounds in studies on orientation of nuclear substituents of furan, has been made available by the synthesis of 5-methyl-3-furoic acid.

AMES, IOWA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Aliphatic Tertiary Alcohols and Chlorides Containing the Normal Amyl Group and the Related Olefins and their Ozonolysis

BY FRANK C. WHITMORE AND F. E. WILLIAMS[1]

The primary purpose of this research was to supply intermediates for the preparation of certain complex pinacolyl alcohols for use in rearrangement studies.[2] The series of tertiary alcohols chosen contained combinations of the five normal alkyls up to amyl with each alcohol containing at least one amyl group. The n-amyl group was chosen because of the present availability of that alcohol in large quantity.[3] Twelve of the fifteen possible alcohols of this type have been prepared in this study. Of these only four have been prepared elsewhere. These are dimethylamylcarbinol,[5] methylethylamylcarbinol,[3] diethylamylcarbinol[3,4] and triamylcarbinol.[6] The triamylcarbinol was kindly supplied by Dr. Marvel. The twelve carbinols were prepared by means of the Grignard reagent in yields of 40–75%. The chief difficulty was in the distillation of the carbinols. All traces of acid had to be removed before distillation and a suitably low pressure was necessary.

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. This study was finished in August 1930.

[2] (a) Whitmore, THIS JOURNAL, 54, 3274, 3431 (1932); (b) Whitmore and Woodburn, *ibid.*, 55, 361 (1933).

[3] The alcohol used in this work was generously supplied by the Sharples Solvents Corporation of Philadelphia.

[4] Masson, *Compt. rend.*, 132, 483 (1901); V. Braun and Sobecki, *Ber.*, 44, 1927 (1911).

[5] Davies, Dixon and Jones, *J. Chem. Soc.*, *131*, *468* (1930).

[6] Moyer and Marvel, "Organic Syntheses," Vol. XI, 1931, p. 100.

The alcohols were all colorless sirupy liquids. The higher ones were entirely odorless. Dimethylamyl and methylethylamyl carbinols had pronounced camphor odors and methylpropylamylcarbinol had a slight odor of similar nature. As the number of simple aliphatic tertiary alcohols is increased[2b] regularities in physical properties are appearing. These will be discussed in a later paper.

The chlorides were prepared by hydrogen chloride in the usual way.[2b] The higher members could not be distilled without decomposition even at pressures below 1 mm. These were successfully purified by shaking with cold concentrated sulfuric acid,

The only one of the alcohols which had been previously converted to an olefin is dimethylamylcarbinol,[7] whose chloride was distilled with solid potassium hydroxide to give 2-methylhexene-2. Of the eleven other carbinols, ten were successfully dehydrated by Hibbert's iodine method. The triamylcarbinol carbonized so badly that its study was abandoned. The alcohols fell in two groups according to their ease of dehydration, (1) those easily dehydrated, methylethylamyl, methylbutylamyl, diethylamyl, ethyldiamyl, and butyldiamyl carbinols, and (2) those which required longer heating, methylpropylamyl, methyldiamyl, propyldiamyl and dipropylamyl carbinols. The fact that the second group contains only alkyls with odd numbers of carbon atoms may or may not be fortuitous. Ozonolysis of the olefins gave ketones which could be isolated and identified but great difficulty was experienced with the aldehyde products? The carbinols, $R(CH_3)(C_5H_{11})COH$, formed olefins which gave as their chief ozonolysis product methyl amyl ketone, indicating that the dehydration involved mainly the ethyl, propyl or butyl group rather than the methyl or amyl group. The olefin from diethylamylcarbinol gave ethyl amyl ketone. Similarly propyl amyl ketone was obtained from dipropylamylcarbinol. Ethyldiamylcarbinol gave ethyl amyl ketone. No products were identified from dibutylamyl, propyldiamyl or butyldiamyl carbinol. Thus the chief dehydration products identified are as follows: methylethylamylcarbinol, 3-methyloctene-2; methylpropylamylcarbinol, 4-methylnonene-3; methylbutylamylcarbinol, 5-methyldecene-4; methyldiamylcarbinol, 6-methylundecene-5; dipropylamylcarbinol, 4-propylnonene-3; ethyldiamylcarbinol, 6-ethylundecene-5.

Experimental

The bromides used in the syntheses of the tertiary alcohols were prepared by the methods of Kamm and Marvel[9] with the following properties and yields: n-propyl bromide, b. p. 70–70.3° (740), 70%; n-butyl bromide (stirring and refluxing for eight

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[7] Henry, *Compt. rend.*, 143, 103 (1906).

[8] This problem has been studied intensively and successfully by J. M. Church in this Laboratory since 1930 and will be reported on shortly

[9] **Kamm** and Marvel, "Organic Syntheses," Vol. I, 1921, p. 5.

hours), b. p. 99–101° (730), 75%; *n*-amyl bromide (from Sharples *n*-amyl alcohol, b. p. 135–136.5° (748)), b. p. 127–128° (736 mm.), 50%. Ethyl caproate was prepared in 53% yield from the acid and alcohol and dry hydrogen chloride, b. p. 163–164° (733). Methyl *n*-amyl ketone (b. p. 148–151° (738), yield 67%) was prepared from ethyl *n*-butylacetoacetate[10] supplied by the Mallinckrodt Chemical Works.

The Grignard reagents were prepared in the usual way.'' The reactions with the carbonyl compounds involved no unusual features except that the reaction product was decomposed by pouring on ice and only a slight excess of dilute sulfuric acid. The last traces of acid were removed from the ether extracts by standing with solid anhydrous sodium carbonate. The alcohols were distilled at 15 mm. or below using a barostat to control the pressure. Heat for the distillations was supplied by an oil-bath. The study of the carbinols is summarized in Table I.

TABLE I

TERTIARY CARBINOLS

Carbinol	Source Carbonyl cpd.	Source Halide	Yield %	Yield g.	Analyses Calcd. C	Analyses Calcd. H	Analyses Found C	Analyses Found H	B. p., °C. (mm.)	n_D^{20d}	d_4^{25d}
Me_2Am	$AmCO_2Et$	MeCl	61	158					66.5–68.5 (15) 162–164 (235)	1.4240	0.8136
MeEtAm	MeCOAm	EtBr	76	650	74.9	14.0	74.9 74.6	14.4 14.5	80–81 (15)"	1.4315	.8258
MePrAm	MeCOAm	PrBr	70	660	75.9	14.0	75.9 76.2	14.6 14.2	92–93 (15)	1.4338	.8245
MeBuAm	MeCOAm	BuPr	66	680	76.7	14.0	76.4 76.5	14.1 14.2	106–107 (15)	1.4369	.8262
$MeAm_2$	MeCOOEt	AmBr	75	420	77.3	14.1	77.7 77.8	13.7 14.1	80–83 (2 0)	1.4392	.8271
Et_2Am	AmCOOEt	EtBr		175	76.9	14.0	76.4 75.1	14.2 14.0	89.5–91.5 (15)	1.4390	.8361
Pr_2Am	AmCOOEt	PrBr	40	250	77.3	14.1	77.3 77.1	14.1 14.2	75–76 (1.4)[b]	1.4406	.8324
Bu_2Am	AmCOOEt	BuPr	76	490	78.4	14.1	78.2 78.0	14.1 14.3	90–92 (1.2)	1.4450	.8345
$EtAm_2$	EtCOOEt	AmBr	40	240	77.9	14.1	77.9 77.9	14.2 14.3	87–89 (2.0)	1.4438	.8348
$PrAm_2$	PrCOOEt	AmBr	58	220	78.4	14.1	78.9 79.1	14.4 14.1	81–82 (0.4)	1.4452	.8336
$BuAm_2$	BuCOOEt	AmBr	59	200	78.9	14.1	78.7 78.4	14.1 14.0	99–102 (1.0)	1.4460	.8344
Am_3	Et_2CO_3	AmBr			79.2	14.1	79.4 79.4	14.1 14.2	115–117 (1.5)	1.4470	.8293[c]

[a] Barostat set at 15 mm. [b] Pressures of 2.0 mm. and lower were measured with a McLeod gage; *cf.* Gross and White, Ind. Eng. *Chem.*, 13, 702 (1921). [c] This low value is unexplained. [d] For methods used see Reference 2b.

The tertiary chlorides were prepared from the carbinols and hydrogen chloride gas.[2b] All the alcohols darkened in the process but this was especially noticeable with diethylamyl- and methylpropylamylcarbinol. This phenomenon has not been explained. Most of the chlorides were distilled at pressures of about 1 mm. (McLeod gage). In several cases this was impossible because of decomposition even at these pressures. Such chlorides were treated as follows. The dissolved hydrogen chloride was removed at room temperature and low pressure. The crude chloride was then washed with one-half volume of concentrated C. P. sulfuric acid. After separating the acid, the cloudy chloride layer was centrifuged until clear. The chloride layer was removed and allowed to stand at 0° for twelve hours with anhydrous sodium sulfate

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[10] Johnson and Hager, "Organic Syntheses," Vol. VII, 1927, p. 60.

[11] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929).

and carbonate. Filtration gave a clear colorless odorless liquid. The analyses of chlorides purified in this way indicated a higher purity than that obtained in the other chlorides which were distilled. The crude chlorides are stable at 0° but at room temperature slowly decompose with the evolution of hydrogen chloride and with darkening. The purified chlorides underwent little or no change in two years. The chlorides are summarized in Table II.

TABLE II

TERTIARY CHLORIDES

Carbinyl chloride	Yield %	Yield g.	Chlorine analyses Calcd.	Chlorine analyses Found	B. p., °C. (mm.)	n_D^{20}	d_4^{25}	Stability[b]
Me_2Am	73	27	23.9	23.7	[a]	1.4257	0.8568	*c*, d, e
MeEtAm	72	68	21.8	21.6	72.7–74 (15)	1.4347	.8680	*c*, d, *e*
MePrAm	85	75	20.1	20.0	43–45 (1.0)	1.4375	.8663	*e*, f, g
MeBuAm	84	81	18.6	18.5	52–54 (0.75)	1.4404	.8645	*c*, *d*, e
$MeAm_2$	33	29	17.3	17.1	63–65 (0.75)	1.4426	.8623	c, d, e
Et_2Am	72	64	20.1	20.1	42-43 (0.5)	1.4423	.8792	c, *e*, g
Pr_2Am	79	70	17.3	17.3	60–62 (0.65)	1.4460	.8699	*c*, d, *e*
Bu_2Am	76	65	15.3	15.2		1.4490	.8666	*e*, *f*, *g*
$EtAm_2$	61	54	16.2	16.0	74–76 (0.65)	1.4474	.8698	*c*, *d*, *h*
$PrAm_2$	67	60	15.3	15.2		1.4490	.8676	*e*, *f*, *g*
$BuAm_2$	83	45	14.4	14.4		1.4507	.8649	*c*, d, *e*
Am_3	70	75	13.6	13.6		1.4511	.8637	

[a] Halides for which no boiling points are given decomposed on heating even below 1 mm. and so were purified by the sulfuric acid method. [b] The samples of chlorides were examined after having stood for two years in ordinary glass bottles in the laboratory. The chlorides proved to be surprisingly stable. The changes on standing follow: [c] Still colorless. [d] No odor of hydrogen chloride. [e] Change in refractive index not over 0.0004. [f] Color changed to yellow. [g] Odor of hydrogen chloride. [h] Increase in refractive index of +0.0008.

TABLE III

OLEFINS

Olefin	Parent carbinol	Yield %	Yield g.	Analyses, calcd. C, 85.6; H, 14.4 Found C	Analyses, calcd. C, 85.6; H, 14.4 Found H	B. p., °C. (mm.)	n_D^{20}	d_4^{25}
3-Methyloctene-2	**MeEtAm**	79	100	83.4	14.6	143–145 (734)	1.4247	0.7409
4-Methylnonene-3 and -4	**MePrAm**	67	94			58–59 (15) 161–163.5 (734)	1.4293	.7483
5-Methyldecene-4	**MeBuAm**	64	66	83.2 85.0	14.7 15.1	75–76 (15)	1.4333	.7578
6-Methylundecene-5	**$MeAm_2$**	59	100	85.8 86.1	14.5 14.8	90–92 (15)	1.4368	.7647
3-Ethyloctene-2	**Et_2Am**	68	48	84.7 85.0	14.9 14.7	57–59 (15)	1.4303	.7545
4-Propylnonene-3	**Pr_2Am**	82	74	85.6 85.3	14.6 14.7	84–87 (15)	1.4362	.7643
$C_{14}H_{28}$[a]	**Bu_2Am**	65	95	85.1 85.3	14.6 14.7	113–115 (15)	1 4414	.7748
6-Ethylundecene-5	**$EtAm_2$**	72	45	86.0 86.1	14.7 14.5	102–105 (15)	1.4401	.7701
$C_{14}H_{28}$[a]	**$PrAm_2$**	50	80	85.0 85.1	14.6 14.8	111–114 (15)	1.4411	.7749
$C_{15}H_{30}$[a]	**$BuAm_2$**	63	57	85.9 86.0	14.6 14.7	126–129 (15)	1.4436	.7781

[a] The ozonolysis products of these olefins gave mixtures of semicarbazones which could not be separated or identified.

The carbinols were dehydrated by heating at 100° with a trace of iodine.[12] The best method for removing traces of iodine was treatment with mercury. The product was distilled under reduced pressure. The results on the olefins are summarized in Table III.

TABLE IV

OZONOLYSIS OF OLEFINS FROM THE TERTIARY CARBINOLS

Parent carbinol	Olefin used, g.	Ozonide obtained, g.	Oil from ozonide, cc.	Main fractions B. p., °C.	Main fractions cc.	Low fractions, cc.	High fractions, cc.	Semicarbazone isolated	M. p., °C.	Mixed m. p., °C.
MeEtAm	25	33	15	145–153	7	4	3	$CH_3COC_5H_{11}$	121–122	121–123
MePrAm	25	31	19	97–101	5	4	4	$CH_3COC_3H_7$(?)		
				145–155	6			$CH_3COC_5H_{11}$	121–122	122–123
MeBuAm	25	31	12	144–154	3 5	5	3	$CH_3COC_5H_{11}$	120–121	121–122
$MeAm_2$	25	31	11	146–152	5	4	2	$CH_3COC_5H_{11}$	121–123	121–123
Et_2Am	25	32	14	165–168	7	5	2	$C_2H_5COC_5H_{11}$[a]	116–117	
Pr_2Am	25	32	15	71–81 (15)	5 5	6	3	$C_3H_7COC_5H_{11}$[b]	72–73	
Bu_2Am	25	31	12	58–95 (15)	6 5	3	1	[c]	58–60	
$EtAm_2$	25	32	15	98–112 (13)	4	9	1	$C_2H_5COC_5H_{11}$(?)	111–112 5	
$PrAm_2$	25	31	13	80–92 (15)	4	2	1	[d]		
				92–105 (15)						
				105–120 (15)						
$BuAm_2$	25	32	19	89–95 (13)	5	2	1	[e]		
				95–105 (13)	7					
				105–118 (13)	4					

[a] Bouveault and Locquin, Bull. *soc. chim.*, [3] **31**, 1158 (1904), give 117–117.5° as the m. p. of the semicarbazone of ethyl n-amyl ketone.

[b] They give 73–74' for the corresponding derivative of n-propyl n-amyl ketone.

[c] The semicarbazone obtained did not correspond to any known substance.

[d] Each fraction gave mixtures of semicarbazones which could not be separated by repeated crystallizations.

[e] The first two fractions gave impure semicarbazones.

The ozonization of the olefins was performed in 29–35° ligroin at –15° with ozonized oxygen.[13] The ozonides, freed from solvent, were surprisingly stable even to boiling water. They were finally decomposed by boiling water and zinc dust.[14] All attempts to identify aldehyde or acid products failed. The ketones could be identified, however, as their semicarbazones. These were confirmed by mixed melting point determinations with known materials. The ozonolysis results are summarized in Table IV.

Summary

1. A series of twelve aliphatic tertiary alcohols of the general types, $R(CH_3)(n\text{-}C_5H_{11})COH$, $R_2(n\text{-}C_5H_{11})COH$ and $R(n\text{-}C_5H_{11})_2COH$, in which R is methyl, ethyl, n-propyl, n-butyl and n-amyl, has been synthesized and studied.
2. The tertiary chlorides have been made from the alcohols.
3. The alcohols have been dehydrated.

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[12] Hibbert, THIS JOURNAL, 37, 1748 (1915).

[13] Cf. Henne, *ibid.*, 51, 2676 (1929); Smith, *ibid.*, 47, 1844 (1925). Full details of the ozonolysis technique as used in this Laboratory will be published shortly by J. M. Church.

[14] Cf. Noller and Adams, *ibid.*, 48, 1077 (1926).

4. Six of the resulting olefins have been identified by their ozonolysis products. These are 3-methyloctene-2, 5-methyldecene-4, 6-methyl undecene-5, 3-ethyloctene-2, 4-propylnonene-3 and 6-ethylundecene-5. In addition a mixture of 4-methylnonene-3 and -4 was identified.

5. Alcohols of the type, $R(CH_3)(n\text{-}C_5H_{11})COH$, were dehydrated chiefly through the R group.

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Solubility Relationships among Optically Isomeric Salts. III. The Mandelates and Alpha-Bromocarnphor-Pi-Sulfonates of Alpha-Phenylethylamine and Alpha-Para-Tolylethylamine

BY A. W. INGERSOLL, S. H. BABCOCK AND FRANK B. BURNS

The following five types of optically isomeric salts represent all the possible combinations of active and inactive acid and base ions.

(*d*B*d*A or *l*B*l*A); (*d*B*l*A or *l*B*d*A); *dl*B*dl*A; (*d*B*dl*A or *l*B*dl*A); (*dl*B*d*A or *dl*B*l*A)

The stabilities and relative solubilities of these types of salts determine which of them can exist in solution, and the order in which the stable salts can be separated from a mixture by fractional crystallization. It has been shown in previous papers[1] that these factors are of primary importance for a method of complete optical resolution in which mixtures containing several varieties of isomeric salts may be encountered. It was shown that not more than three of the nine varieties of salts represented above can result from the evaporation of a solution, no matter what proportions of active and inactive acid and base ions may have been introduced originally. Nevertheless, it was pointed out that there are some twenty[2] different orders in which these coexistent salts may separate during fractional crystallization. At present it seems impossible to predict the stabilities and relative solubilities of the salts of a particular acid and base. Hence numerous groups of isomeric salts are being studied for the purpose of gaining a comprehensive knowledge of these factors. Five such groups of salts have already been described and classified. This paper describes a similar study of the four additional groups of salts named in the title.

The salts previously described illustrated two instances each of Cases 4[1a] and 7[1b,1d] and one of Case 8.[1c] The salts described in this paper were found to illustrate the previously unobserved cases (1) and (6), another instance of Case 8, and an instance of either Case 4 or 7, depending on the

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(1) (a) Ingersoll, THIS JOURNAL, **47**, 1168 (1925); (b) 60, 2264 (1928); (c) Ingersoll and White, ibid., **54**, 274 (1932); (d) Ingersoll and Burns, ibid., 64, 4712 (1932).

(2) Only eight orders (Cases 1–8) are possible in the mixtures resulting from the usual procedure for complete resolution. All of the cases were described and numbered in Part I.[1c]

procedure. Thus the mandelates of a-phenylethylamine were found to include four stable types of salts in the solubility order

(*d*B*l*A or *l*B*d*A) < (*dl*B*d*A or *dl*B*l*A) < *dl*B*dl*A < (*d*B*d*A or *ZBZA)*

When the partially active base (*dl*B + *l*B) was combined with the dl-acid the system *l*B*d*A<*dl*B*dl*A<*l*B*l*A (Case 4) resulted; when partially active acid (*dl*A + *d*A) was combined with the dl-base the system *dl*B*d*A<*dl*B*dl*A (Case 7) resulted. Both procedures permitted the purification of active acid and active base. Cases 4 and 7 have been observed previously, but the order of solubility for the four salts is new. It may be noted that the modified procedure for complete resolution would place the resulting salts in the favorable cases (10) or (15) depending on the proportions of active and inactive acid and base.

The mandelates of the closely related base, a-p-tolylethylamine, were then studied and the order of solubility was found to be

*dl*B*dl*A < (*d*B*l*A or *l*B*d*A) < (*d*B*d*A or *l*B*l*A)

Thus, while the acid and base were reciprocally resolvable, only the inactive forms could be obtained pure from partially active specimens by either the usual or the modified procedure. This is the first example of an authentic Case 6. Perkin and Robinson[3] found a similar order of solubility in ethyl acetate for the corresponding a-bromocamphor-a-sulfonates of narcotine, but did not examine the (*d*B*dl*A or *l*B*dl*A) type of salt. Hence their salts cannot be definitely classified as Case 6.

The a-bromocamphor-a-sulfonates of a-phenylethylamine were found to exhibit the solubility order

*dl*B*dl*A < (*d*B*dl*A or *l*B*dl*A) < (*d*B*l*A or *l*B*d*A) < (*d*B*d*A or *l*B*l*A)

Thus the dl-base can be resolved by the active forms of the acid,[4] but the dl-acid was found to form stable partially racemic salts with the active forms of the base. The order of solubility corresponded to Case 8 in the usual procedure and would have given cases (19) or (20) in the modified procedure. All of these cases are unfavorable for the purification of salts containing active ions. A similar solubility order for four salts has not previously been encountered.

It was shown in a recent paper[5] that dl-a-bromocamphor-a-sulfonic acid was resolved by the active forms of a-p-tolylethylamine. It has now been found that the dl-base can also be resolved, though not so readily, by the active forms of the acid. The stable salts were in the solubility order

(*d*B*d*A or *l*B*l*A) < (*d*B*l*A *or* *l*B*d*A) < *dl*B*dl*A

This is the first observed instance of Case 1.

The above results show that even two bases as closely related as α-phenylethylamine and α-*p*-tolylethylamine form entirely different systems

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(3) Perkin and Robinson, *J. Chem. Soc.*, 99, 788 (1911).

(4) Hunter and Kipping, *ibid.*, 88, 1147 (1903).

(5) Ingersoll and Babcock, THIS JOURNAL, 55, 341 (1933).

of salts with mandelic acid, and that these systems are again quite different from those formed from the same bases and α-bromocamphor-π-sulfonic acid. Hence it would not be safe to predict that the isomeric salts of structurally similar bases or acids should be similar in their stabilities and relative solubilities. It may be noted also that the order of solubility among all of the stable salts in each group has been found to be different in eight of the nine groups thus far described. In six of these the solubilities were favorable for the application of the method for complete resolution in its usual form. More groups of salts must be studied before the relative frequency of occurrence of the various cases can be estimated, though thus far Cases 4 and 7 have appeared rather often.

Experimental

α-Phenylethylamine Mandelates.—The resolution of dl-mandelic acid with d- and l-a-phenylethylamine has been briefly described by L. Smith.[6] The intermediate salts were not described. Since this method appears to be more satisfactory than any other given in the literature, it is briefly described here. dl-Mandelic acid (38 g.) was combined with 30 g. of d-a-phenylethylamine in 350 cc. of hot water and the solution cooled. The first fraction, when recrystallized three times from about four parts of water, was practically pure *d*B*l*A salt. By systematically working the mother liquors 29.5 g. (86%) of this salt was obtained. For analysis the salt was recrystallized from 95% ethanol.

d-α-**Phenylethylamine**-*l*-**mandelate** formed elongated hexagonal plates or flattened prisms, m. p. 177° (corr.), and was anhydrous. The solubility was 4.91 g. per 100 g. of water at 30°.

Rotation. Subs. 1.7486 g. made up to 50 cc. in water gave α^{25}_{D} $-4.23°$ in 2 dm.; $[\alpha]^{25}_{\mathrm{D}}$ $-60.4°$, $[\mathrm{M}]_{\mathrm{D}}$ $-165°$ $(10)^2$.

A sample of the salt was decomposed with a small excess of concentrated hydrochloric acid and the mandelic acid extracted with ether. After one crystallization from water with decolorizing carbon it melted at 133° and had $[\alpha]^{25}_{\mathrm{D}}$ -154.8 (5% in water) in close agreement with published values. The active base was recovered by making the hydrochloric acid solution alkaline and distilling with steam. The distillate thus obtained was used directly in the next run.

d-α-**Phenylethylamine**-*d*-**mandelate.**—The mother liquors from the separation of the *d*B*l*A salt became sirupy and discolored on concentration and slowly set to a mass from which the *d*B*d*A salt could not be obtained pure. This salt was therefore prepared from its pure components, but remained somewhat sticky and discolored slightly on drying. The solubility was about 18 g. per 100 g. of water at 30° and the molecular rotation was about $+180°$ $(10)^2$. These values are slightly inaccurate but the salt is certainly the most soluble one of the group.

dl-α-**Phenylethylamine**-*d*-**mandelate.**—The partially resolved mandelic acid (*dl*A + *d*A) was recovered from the mother liquors of the resolution and crystallized once from the least possible amount of water. The crystalline fraction (principally *d*-mandelic acid) was reserved and the mother liquor, which then contained about 17 g. of mandelic acid, [a], +48.5, was neutralized with *dl*-α-phenylethylamine. The resulting salts formed the system *dl*B*d*A < *dl*B*dl*A and the partially racemic salt (5.2 g.) was obtained by systematic crystallization from water. After crystallization from 95% ethanol and again from water it formed large, transparent plates, m. p. 176° (corr.), and was anhydrous. The solubility was 5.81 g. per 100 g. of water at 30°.

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[6] Smith, *J. prakt. Chem.*, [2] **84**, 743 (1911).

Rotation. Subs., 1.3904 g. made up 50 cc. in water gave α^{25}_{D} +3.53 in 2 dm.; $[\alpha]^{25}_{D}$ +63.5°, $[M]_D$ +174° (10)^2.

The mandelic acid was recovered from this salt with ether as described for the *d*B*l*A salt, washed with a little water and dried. It then melted at 131° and had $[\alpha]^{25}_{D}$ +152.5° (3% in water). The recovered base was inactive.

dl-a-Phenylethylamine-dl-mandelate.—The mother liquors from the separation of the *dl*B*d*A salt deposited a mass of small crystals consisting largely of the *dl*B*dl*A salt. A sample melted at 133" and was faintly dextrorotatory. The pure salt was therefore made from its components. It formed small plates, m. p. 138° (corr.), and was anhydrous. The solubility was 12.29 g. per 100 g. of water at 30°.

2-a-Phenylethylamine-d-mandelate.—In a separate experiment 30 g. of the partially active amine (*dl*B 80% + *l*B 20%) was combined with 38 g. of dl-mandelic acid and the salts fractionated. The system *l*B*d*A < *dl*B*dl*A < *l*B*l*A resulted. After prolonged fractionation 3.2 g. of pure *l*B*d*A salt (calcd. 6.8 g.) was obtained. This had $[\alpha]^{25}_{D}$ +58.9° and otherwise closely resembled the *d*B*l*A salt described above. The intermediate fractions were faintly dextrorotatory and the final mother liquors strongly levorotatory.

α-*p*-Tolylethylamine Mandelates.—The base used in the following experiments was prepared and resolved by a recently described modification[1d] of the method of Stenberg.[7]

dl-a-p-Tolylethylamine-dl-mandelate.—A quantity (13.5 g.) of partially active base (*dl*B + dB, [a], +19°) was combined with dl-mandelic acid (15.2 g.) in 100 cc. of hot water and the salts fractionally crystallized. After six recrystallizations the head fraction, which at first was levorotatory, became inactive. The salt (8.2 g.) formed transparent prisms or rhomboidal plates, m. p. 136° (corr.), and was anhydrous. It was identical with the salt prepared from equivalent amounts of the dl-base and dl-acid. The solubility was 4.89 g. per 100 g. of water at 25°.

d-α-*p*-Tolylethylamine-*l*-mandelate.—The intermediate fractions from the crystallization described above contained a salt only slightly more soluble than the *dl*B*dl*A salt. From the maximum rotation observed (−41°) this appeared to be the impure *d*B*l*A salt. In a separate experiment this salt was prepared from the pure components. It formed slender prisms, m. p. 146° (corr.) and was anhydrous. The solubility was 5.18 g. per 100 g. of water at 25°.

Rotation. Subs., 1.3963 g. made up to 25 cc. in water gave $[\alpha]^{25}_{D}$ −6.42° in 2 dm.; $[\alpha]^{25}_{D}$ −57.5°, $[M]_D$ −165° (10)^2.

d-α-*p*-Tolylethylamine-*d*-mandelate.—The foot fractions from the crystallization described above yielded crops of dextrorotatory needles (maximum rotation +24°) but the *d*B*d*A salt could not be obtained pure from the mixture. It was therefore prepared from its components. It formed small needles, m. p. 140" (corr.), and was anhydrous. The solubility was 7.12 g. per 100 g. of water at 25°.

Rotation. Subs., 1.2345 g. made up to 25 cc. in water gave $[\alpha]^{25}_{D}$ +6.45° in 2 dm.; $[\alpha]^{25}_{D}$ +65.3°, $[M]_D$ +188°(10)^2.

l-x-*p*-Tolylethylamine-*l*-mandelate.—This salt was made from the pure components. It melted at 140" (corr.), had $[\alpha]^{25}_{D}$ −65.0°, and was otherwise closely similar to the *d*B*d*A salt.

Instability of *dl*B*d*A or *dl*B*l*A Type.—A small-scale experiment was made to determine whether the dl-base could be resolved with I-acid. The salt formed from these was fractionated and finally gave three successive fractions having rotations —61.3, —62.3 and −64.8°, respectively. The base liberated from the head fraction was dextrorotatory, that from the foot fraction levorotatory. The resolution therefore occurred, but appeared too tedious for practical use and was not further studied.

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(7) Stenberg, *Z. physik. Chem.*, **70**, 534 (1910).

α-Phenylethylamine-α-bromocamphor-π-sulfonates.—The pure *l*B*d*A salt and the impure *d*B*d*A salt of this series have been prepared by Hunter and Ripping[4] by the partial resolution of the dl-base with the d-acid. This work was repeated. The dl-a-bromocamphor-r-sulfonic acid required for the study of the other types of salts has been described in a recent paper.[5]

l-α-Phenylethylamine-d-α-bromocamphor-π-sulfonate.—This salt formed large, transparent prisms, m. p. 205° (corr.), and is anhydrous. These properties and the rotation, $[\alpha]^{25}_{D}$ +62.6°, $[M]_D$ +270°(10)^2, agreed with the data of Hunter and Kipping. The solubility was found to be 5.40 g. per 100 g. of water at 25°.

d-α-Phenylethylamine-d-α-bromocamphor-π-sulfonate.—This salt was not obtained completely pure during the resolution referred to above. Also an attempt to prepare it from its components gave a dense mass of needles that could not be entirely freed from the sirupy mother liquor. The salt after drying at 100" melted at 183–186° and had $[\alpha]^{25}_{D}$ +63.3°. It was by far the most soluble type of salt in the group.

dl-α-Phenylethylamine-dl-α-bromocamphor-π-sulfonate.—This salt was prepared from the ammonium salt of the dl-acid and an acetic acid solution of the dl-base. It separated from water as coarse needles which melted at 155° (corr.) after drying at 110°. It was probably the monohydrate, but a sample kept for several weeks became anhydrous. The solubility of the hydrated salt was 2.05 g. per 100 g. of water at *25".*

Anal. Calcd. for $C_{18}H_{26}O_4NSBr\cdot H_2O$: H_2O, 4.00. Found: H_2O, 3.47 (air-dry salt).

d-α-Phenylethylamine-dl-α-bromocamphor-π-sulfonate.—This salt was formed in an attempt to resolve the dl-acid with d-base. The resulting salt was crystallized from water, 95% ethanol, moist ethyl acetate, and chloroform under various conditions but was not thereby resolved. It formed massive prisms from water or ethanol and was probably the monohydrate. The solubility of this was 3.11 g. per 100 g. of water at 25". The anhydrous salt melted at 170° (corr.).

Anal. Calcd. for monohydrate: H_2O, 4.00. Found: H_2O, 3.64.

Rotation. Subs., 1.4505 g. (anhydrous) made up to 50 cc. in water gave $[\alpha]^{25}_{D}$ +0.07° in *2* dm.; $[\alpha]^{25}_{D}$ +1.20, $[M]_D$ +5.2°(10)^2.

a-p-Tolylethylamine-a-bromocmphor-r-soate — The resolution of the *dl*-acid with the I-base and the pure *l*B*l*A and lBdA salts were described in a recent paper.[5] For convenience in comparison these salts are briefly described here.

*l*B*l*A·H_2O formed coarse prisms, $[\alpha]^{25}_{D}$ −62.7°, $[M]_D$ −291°(10)^2. Solubility 2.10 g. Anhydrous salt m. p. 165° (corr.).

*l*B*d*A·H_2O formed needles; after drying these had $[\alpha]^{25}_{D}$ +59.4°, $[M]_D$ +265°(10)^2. Solubility (hydrated salt) 2.96 g. Anhydrous salt m. p. 232° (corr.).

Resolution of dl-Base **with** d-Acid.—The base (67.5 g.) in dilute acetic acid was combined with ammonium *d*-α-bromocamphor-π-sulfonate (130 g.) in 1 liter of hot water and the salts fractionated. Although the salts (*d*B*d*A and *l*B*d*A) are the same *types* as those described above, they could not be separated with equal ease. Apparently the partially racemic salt, which in this case would be ***dl*B*d*A**, was considerably more stable than the *l*B*dl*A type from which the salts *l*B*l*A and lBdA were formed. Fractionation was conducted, as previously described, by allowing the first fraction to separate from about seven parts of water at 80 to 50° and the remaining material from 50° to room temperature. Similar fractions were then combined and recrystallized similarly. In this way an apparently homogeneous head fraction (80 g.) and a fraction consisting of the pure lBdA salt (52 g.) were obtained. The lBdA salt was practically identical in properties with the salt described above, but the head fraction melted at 162°, had $[\alpha]^{25}_{D}$ \$63.4" and solubility 2.67 g. at 25°. The base obtained from it had $[\alpha]^{25}_{D}$ +28.2° instead of the value +34 6° previously obtained. When the salt was recrystallized repeatedly at 80 to 55° there was finally obtained 54 g. of pure *d*B*d*A salt. The intermediate crops were not further fractionated since this base can be much more easily resolved by means of d-camphoric acid.[1d]

d-α-*p*-**Tolylethylamine**-*d*-α-**bromocamphor**-π-**sulfonate.**—This salt crystallized as monohydrate in transparent prisms; solubility 2.12 g. per 100 g. of water at 25°; m. p. (anhydrous) 165° (corr.).

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$; H_2O, 3.87. Found: H_2O, 3.89.

Rotation. Subs., 0.9280 g. (hydrated) made up to 50 cc. in water gave $[\alpha]^{25}_D$ +2.32° in 2 dm.; $[\alpha]^{25}_D$ +62.5°, $[M]_D$ +290°(10)².

dl-α-*p*-**Tolylethylamine**-*dl*-α-**bromocamphor**-π-**sulfonate.**—This salt was prepared from the inactive components. It first separated as an oil, which solidified. It crystallized from water in anhydrous needles, m. p. 161° (corr.). The solubility was 3.38 g. per 100 g. of water at 25°.

Summary

1. The resolution of dl-mandelic acid by an improvement of the method of Smith[R] has been described.

2. All of the stable isomeric mandelates and α-bromocamphor-π-sulfonates of a-phenylethylamine and a-p-tolylethylamine have been described and classified according to their stabilities and relative solubilities.

3. The significance of these factors for the separation of mixtures of optically isomeric salts has been discussed.

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The Acetoacetic Ester Condensation. IV. The Reaction Product of Certain Aliphatic Esters and Sodium Ethoxide

BY JOHN M. SNELL AND S. M. MCELVAIN

During the course of a study of the reaction of metallic sodium on various aliphatic esters[1] a product, which from its boiling point and method of isolation was thought at first to be ketene acetal,[2] was obtained in a small yield from the reaction of sodium and ethyl acetate in absolute ether. Further investigation of this product, however, showed it to be merely a mixture of alcohol and xylene. The latter compound had been used to powder the sodium for the reaction and, presumably, had not been completely removed from the metal by ether washing, for in subsequent experiments when the powdered sodium, after decantation of the xylene, was washed more thoroughly with ether no product was obtained at the point

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(1) Snell and McElvain, THIS JOURNAL, 53, 750 (1931); John M. Snell, Ph.D., Thesis, University of Wisconsin, 1932.

(2) (a) Scheibler and Zeigner, *Ber* , 55, 801 (1922): (b) Scheibler and Marhenkel, Ann., 468, 15 (1927).

where ketene acetal should appear. It was decided then to attempt the preparation of a ketene acetal by the improved method described by Scheibler, Marhenkel and Nikolic.[3] Several attempts, in which the directions of these authors were followed in every detail, to duplicate this preparation were unsuccessful.

In the view of these failures to obtain ketene acetal it seemed advisable to examine Scheibler's so-called "primary reaction product," *i. e.*, the residue left after evaporation of the ester and ether from the sodium ethoxide. This was done using ethyl acetate and ethyl isobutyrate as representative esters.

Experimental Part

Materials Used.—The sodium ethoxide was prepared as recommended by Scheibler, Marhenkel and Nikolic[3] by treating powdered sodium under ether with the theoretical amount of absolute alcohol. The product obtained was white and granular and contained 33.75% Na; calcd. for C_2H_5ONa, 33.80. The ether and esters were purified by washing with water, drying over calcium chloride (in the case of ether) or potassium carbonate (in the cases of the esters). Each of these materials was then allowed to stand over phosphorus pentoxide for twenty-four hours and then distilled directly from this reagent.

An Attempted Preparation of Ketene Acetal.—The following procedure describes in detail a representative attempt to prepare ketene acetal from ethyl acetate and sodium ethoxide according to the procedure described in the literature.[3] Twenty-three grams (1 atom) of sodium was finely powdered in a 1-liter round-bottomed flask by shaking under heated xylene. After cooling and decantation of the xylene the powdered metal was washed thoroughly with four or five portions of absolute ether, and then covered with 500 cc. of fresh ether. A reflux condenser was fitted to the flask and 50 g. (1.1 mole) of absolute alcohol was slowly run in from a dropping funnel at the top of the condenser. The reactants were protected by calcium chloride tubes from atmospheric moisture. After all the alcohol had been added the mixture was allowed to stand for fifteen hours or longer. Then 200 g. (2.2 moles) of ethyl acetate was added. At this point cooling the flask, as recommended by the original investigators,[3] was unnecessary as no perceptible heat was generated. The mixture was allowed to stand with occasional shaking for twenty-four hours, and then was poured into a shallow dish and placed in an empty vacuum desiccator. The volatile substances were removed by evacuation with a water pump, a calcium chloride tower being interposed to prevent backward diffusion of water vapor. The dry residue (which generally weighed 90–100 g. as compared to 125 g., the weight of reaction product obtained by the original investigators[3]) was scraped from the walls of the dish and the desiccator, pulverized in a porcelain mortar, and triturated with 125 g. of ice water. The resulting solution was extracted with ether in a continuous extraction apparatus[4] for twelve hours, the solvent vapors passing through a 25-cm. spiral Widmer column on the return path to the extraction vessel The ether solution was shaken intermittently for three or four hours with three successive portions of powdered calcium chloride and then washed with a small volume of a saturated solution of calcium chloride. After standing overnight with anhydrous sodium sulfate the ethereal extract was distilled through the Widmer fractionating column mentioned above. It all passed over at 34–35°. Ketene acetal was reported[3] as boiling at 77–78".

Preparation of the "Primary Reaction Product" from Ethyl Acetate.—Seventeen

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(3) Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 28 (1927).

(4) "Organic Syntheses," 1923, Vol. III, p. 88.

grams (0.25 mole) of sodium ethoxide (33.75% Na), under 200–225 cc. of dry ether was treated with 55 g. (0.625 mole) of ethyl acetate and the mixture allowed to stand in a stoppered flask under nitrogen for a period of two to three days with occasional shaking. The ether and ester were then evaporated off under reduced pressure and the residue allowed to stand in a vacuum desiccator over sulfuric acid until it attained a constant weight.

Method of Examination.—The sodium content of the reaction product was determined in the following manner. A sample of approximately 0.25 g. was accurately weighed into a tared porcelain crucible and treated with 0.2 cc. of concentrated sulfuric acid added from a graduated 1-cc. pipet. The crucible was heated gently until most of the volatile matter was expelled and then ignited for thirty minutes in the full flame of a Bunsen burner. The residue was weighed as Na_2SO_4.[5]

In the case of ethyl acetate the only other constituent of the reaction product determined was the sodium derivative of acetoacetic ester. This was estimated by adding about 1 g. of the reaction product to 10 g. of ice, acidifying the resulting solution with acetic acid and extracting with ether. The ether extract was washed until neutral with sodium bicarbonate solution and then made up to 100 cc. with 95% alcohol. A 10-cc. aliquot was treated with 4 drops of a 10% ferric chloride solution and the color compared in a Duboscq colorimeter with that produced by a standard solution of acetoacetic ester in 95% alcohol. This method is accurate to 2–3% if the following precautions are observed, (a) the solutions being compared should be of about the same concentration, (b) the same amount of ferric chloride should be added to equal volumes of the two solutions, (c) the comparisons should be made as soon as possible after the addition of the ferric chloride. A rather imperfect check on this method of estimation was the determination of the amount of 1-*p*-nitrophenyl-3-methyl-5-pyrazolone[6] obtained from an aliquot of the acetoacetic ester solution by the action of *p*-nitrophenylhydrazine. This value was about 70% of that obtained by the colorimetric estimation.

Preparation of the Primary Reaction Product from Ethyl Isobutyrate.—To 6.8 g. (0.1 mole) of sodium ethoxide under 90 cc. of ether was added 29 g. (0.25 mole) of ethyl isobutyrate, and the procedure described above for ethyl acetate followed. In the case of ethyl isobutyrate, however, it was necessary to heat the residue from the evaporation of the ether and ester to a temperature of 100° on a steam-bath for one hour under diminished pressure in order that the excess ester might be completely removed and the residue attain constant weight.

A reaction product was also prepared from ethyl isobutyrate by heating 6.8 g. of sodium ethoxide with 29 g. of the ester alone on a steam-bath for twenty-four to forty-eight hours. The ester was removed by distillation and the residue heated for three hours at 100–150° under diminished pressure. During the distillation of the ester and the heating of the residue the side arm of the receiving flask was connected to a coil condenser cooled in a mixture of ether and solid carbon dioxide. About 1 g. of a mixture of alcohol and ethyl isobutyrate was condensed in this trap.

In addition to the determination of the sodium content of the reaction product, the amount of sodium isobutyrate present was estimated by treating a 5–7 g. sample of the dry reaction product with 50 cc. of water, acidifying with phosphoric acid and distilling the isobutyric acid. This distillate was then titrated with standard alkali. The identity of the isobutyric acid was established by converting it into the *p*-phenylphenacyl ester by the method of Drake and Bronitsky.[7] This ester, which has not been described previously, melts at 88.5°. Calcd. for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38. Found: C, 76.61; H, 6.38.

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(5) Cf. Adickes, *Ber.*, 60, 274 (1927).

(6) Altschul, *ibid.*, 25, 1853 (1892).

(7) Drake and Bronitsky, THIS JOURNAL, 52, 3716 (1930).

The results which were obtained from the examination of the various reaction products, prepared as described above, are summarized in the table. The values of sodio-acetoacetic ester in column 5 are calculated from the colorimetric estimation of acetoacetic ester and the percentages of sodium isobutyrate in column 6 are calculated from the amount of isobutyric acid found by titration. The corresponding values for sodium acetate were not determined. Column 7 represents the calculated percentage of sodium which would be present in the reaction product if it consisted only of the product determined (sodio-acetoacetic ester or sodium isobutyrate) and sodium ethoxide.

ANALYSES OF THE REACTION PRODUCTS FROM ETHYL ACETATE AND ISOBUTYRATE WITH SODIUM ETHOXIDE

Run	Ester ethyl	Solvent	Total % Na in reaction product	% Na acetoacetic ester in reaction product	% RCOONa in reaction product	Total % Na calcd. as $NaOC_2H_5$ and determined component
1	Acetate	Ether	30.24	12.0	?	31.56
2	Acetate	Ether	32.35	5.5	?	32.77
3	Isobutyrate	Ether	33.50	...	0.50	33.74
4[a]	Isobutyrate	None[c]	32.90	...	6.8	32.92
5[b]	Isobutyrate	None[c]	32.80	...	6.5	32.96
6[a]	Isobutyrate	None[c]	32.80	...	5.2	33.10
7[a]	Isobutyrate	None[c]	32.80	...	6.6	32.84

[a] Allowed to react twenty-four hours at 100°. [b] Allowed to react forty-eight hours at 100°. [c] Excess of ester used in these runs.

Discussion of Results

The failure to obtain ketene acetal from the reaction of sodium ethoxide and ethyl acetate in this work must be due to one of the following causes: (a) the present authors do not possess the manipulative skill necessary for the isolation of such a compound, (b) the directions of the original investigators are not sufficiently precise, or (c) the compound in question is not formed in the reaction. Further work along this line by other investigators should show which of these alternatives is responsible for the present disagreement of results. In this connection it should be noted that Arbusow[8] has recently reported his failure to duplicate Scheibler's preparation of carbon monoxide acetal.

It is seen from the data in the above table that in the case of ethyl acetate the values for the sodium content of the reaction product calculated on the assumption that it contains only sodio-acetoacetic ester and sodium ethoxide are only slightly higher than those actually found. This difference is due, in all probability, to small amounts of sodium acetate which were not determined because of the complication introduced by the presence of the acetoacetic ester. With ethyl isobutyrate, however, the absence of the β-keto ester makes possible the accurate determination of

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(8) Arbusow, *Ber.*, **64**, 698 (1931)

the isobutyric acid in the reaction product. The very close agreement between the calculated values of column 7 and the found values in column 4 definitely shows that these reaction products are simply sodium ethoxide mixed with a small amount of sodium isobutyrate.[9]

These data also confirm the contention made by Adickes[10] in a recent publication that such esters as ethyl acetate and isobutyrate form no stable, isolable compounds with sodium ethoxide. That there is no ester, either combined or adsorbed, in the reaction product from ethyl isobutyrate is shown not only by the above analyses but also by the fact that careful fractionation of the ester which was removed from the reaction product during its preparation gave small amounts of lower boiling fractions consisting of a mixture of ester and alcohol and which contained quantities of alcohol (estimated from the saponification value) approximately equivalent to the sodium isobutyrate present in the reaction product. No product other than alcohol and the ester could be found in these lower boiling fractions.

On the basis of these results it seems safe to conclude that the "primary reaction product" (which contains 11.6% Na when derived from ethyl acetate) postulated by Scheibler and co-workers[11] as an intermediate for both the acetoacetic condensation and ketene acetal formation, does not exist. Earlier evidence has been submitted[12] that the precursor, an ester enolate ($RCH{=}C(ONa)OC_2H_5$), of this intermediate is not formed by the action of sodium ethoxide on such esters. The data for ethyl acetate do not absolutely preclude the presence of a small amount of such an intermediate in the reaction product, but in the case of ethyl isobutyrate the data definitely do indicate the absence of such a compound. Consequently, the claim that ethyl isobutyrate undergoes a reaction with sodium ethoxide to form such a reaction product and that this product is converted by hydrolysis into the corresponding ketene acetal[13] cannot be reconciled with the data presented in the present paper.

Summary

All attempts to prepare a ketene acetal by the directions given by Scheibler and co-workers have been uniformly unsuccessful.

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[9] The manner in which the sodium salt of the acid was formed is unknown. It may have resulted from traces of moisture present in the ester or entering the reaction mixture during the course of the reaction, although this hardly seems likely in view of the precautions which were taken to exclude moisture. Scheibler [*Ber.*, **65**, 998 (1932)] has reported the formation of sodium benzoate from the reaction of ethyl benzoate and sodium ethoxide, thus $C_6H_5COOC_2H_5 + C_2H_5ONa \longrightarrow C_6H_5COONa + C_2H_5OH + C_2H_4$. It is possible that a similar reaction is responsible for the sodium isobutyrate obtained in the present work. However, for the purpose of the present discussion the origin of this product is immaterial.

[10] Adickes, *Ber.*, **65**, 522 (1932)

[11] Scheibler and Marhenkel, *Ann.*, **458**, 5 (1927).

[12] McElvain, THIS JOURNAL, **61**, 3124 (1929).

[13] Scheibler and Friese, *Ann.*, **445**, 149 (1925); Scheibler and Marhenkel, *Ann.*, **468**, 14 (1927). However, these authors do not describe the properties of this particular ketene acetal.

An examination of the dry, solid residues remaining after the reaction of ethyl acetate and ethyl isobutyrate with sodium ethoxide has been made and from the results obtained the conclusion is drawn that the so-called "primary reaction product" postulated by Scheibler as the intermediate in the acetoacetic ester condensation and ketene acetal formation does not exist.

MADISON, WISCONSIN

RECEIVED AUGUST 12, 1932
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Notes

Aryl *p*-Bromobenzenesulfonates as Derivatives for the Identification of Phenols

BY VLADIMIR C. SEKERA

In connection with the work on the higher alkyl sulfonates[1] one or two aryl esters were prepared. These beautifully crystalline compounds were so readily prepared and so easily purified that further examples were characterized in order to show their value as derivatives for identification of phenols.

The general method of preparation consisted of mixing equimolecular quantities of the phenol and *p*-bromobenzenesulfonyl chloride with about four equivalents of pyridine and stirring the mixture for about three hours at 15° or lower. With small quantities, less time was needed for the reaction. The reaction mixture was decomposed with ice water containing enough dilute hydrochloric acid to combine with the pyridine. The aryl sulfonate was collected on a Buchner funnel and air dried. One recrystal-

TABLE I

SOME ARYL p-BROMOBENZENESULFONATES

Phenol	Yield, %	M. p., °C.	Anal., % Br Calcd.	Anal., % Br Found
Phenol	86	115.5	25.5	25.5
a-Naphthol	81	104	22.0	21.9
β-Naphthol	69	151–152	22.0	22.4
o-Cresol	75	78–79	24.4	24.6
m-Cresol	74	69–70	24.4	24.3
p-Cresol	76	100	24.4	24.5
o-Nitrophenol	70	97–98	22.3	22.6
m-Nitrophenol	70	108–109	22.3	22.4
p-Nitrophenol	69	112	22.3	22.6
o-Bromophenol	57	125	40.8	41.0
Thymol	71	103.5	21.6	21.5
Guaiacol	61	103–104	23.3	23.6
2,4,6-Tribromophenol	85	139–140	58.1	58.4

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[1] Sekera and Marvel, THIS JOURNAL, 55,345 (1933).

lization from alcohol using a little decolorizing carbon usually gave a pure product. Table I contains a description of these compounds.

CONTRIBUTION FROM THE
CUEMICAL LABORATORY OF THE
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RECEIVED JULY 20, 1932
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Note on the Occurrence of Dehydrodeguelin and Dehydrotoxicarol in Some Samples of Derris Root

BY E. P. CLARK AND GEORGE L. KEENAN

On several occasions during the past two years, specimens of derris root were encountered which yielded no rotenone, but gave instead mixtures of yellow crystals whose melting points ranged from 200 to 225°. After purification by recrystallization from various solvents, these materials gave mixtures of dehydrodeguelin and dehydrotoxicarol. The identity of the substances was proved by the optical immersion method. In two instances, dehydrotoxicarol predominated so that it was possible by fractional crystallization to isolate this substance in an analytically pure condition and identify it by comparison with an authentic sample as to melting point, mixed melting point and optical properties. The materials remaining in the mother liquors were recovered and after recrystallization were shown to consist of mixtures which were impossible to resolve but which when examined by the optical method referred to above were conclusively shown to be essentially dehydrodeguelin and dehydrotoxicarol.

Recently there was obtained from a manufacturer of rotenone an interesting sample of yellow crystals derived from derris root which yielded no rotenone. Upon recrystallization this material yielded a beautiful yellow preparation which melted sharply at 217°. Repeated recrystallizations from various solvents failed to alter the melting point, and it was thought that possibly it was a dehydro derivative of an isomer of deguelin or rotenone. Upon subjecting the material to hydrolysis with alcoholic alkali, an acid corresponding to derrisic acid was readily obtained but it melted at 178° (derrisic acid melts at 158° while deguelic acid melts at 186°). The melting point of this acid did not change after several recrystallizations, which was in harmony with the assumption stated above, especially since analysis of the acid showed its molecular formula to be the same as that of derrisic acid. In the meantime, oxidation of the dehydro derivative (m. p. 217°) with permanganate in acetone and in alkaline aqueous solutions, and also with alkaline hydrogen peroxide, yielded 2-hydroxy-4,5-dimethoxybenzoic, nicouic, risic and derric acids.[1] These facts, especially the isolation of nicouic acid in essentially the same yield as is obtained from dehydrodeguelin, proved that at least the greater part of the original

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(1) Clark, THIS JOURNAL, 54, 3000 (1932)

preparation was dehydrodeguelin. Repeated recrystallization from toluene of the acid which melted at 178° was then undertaken, and its melting point was finally raised to 186°. It was then shown by its melting point, mixed melting point and optical properties to be deguelic acid.

A careful examination of the original dehydro compound by the optical immersion method then revealed that it consisted of dehydrodeguelin and dehydrotoxicarol. This observation is of interest in that the mixture of the two substances was such that it could not be resolved by repeated recrystallization, and it possessed a sharp melting point. It may be possible that such conditions as here presented were responsible for the recording by the earlier workers upon derris root of various yellow compounds which melted in the range between 200 and 230°.[2,3,4] It is of further interest that dehydrotoxicarol has not hitherto been reported as a natural plant constituent, and it was only recently that Merz[5] reported for the first time the natural occurrence of dehydrodeguelin in the seeds of *Tephrosia vogelii*.

(2) Sillevoldt, Ned. *Tijd. Pharm.*, *11*, 246 (1899); Arch. *Pharm.*, 237, 595 (1899).

(3) Tattersfield and Roach, *Ann. Appl. Biol.*, *10*, 1 (1923).

(4) Power, *Pror. Am. Pharm. Assoc.*, 50, *296* (1902): *Pharm. Arch.*, 5, 145 (1902); 6, 1 (1903).

(5) Merz, *Arch. Pharm.*, *270*, 362 (1932).

CONTRIBUTION FROM THE INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
AND THE MICROANALYTICAL LABORATORY
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D. C.

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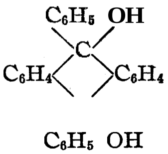
Furan Reactions. V. Derivatives of Furfuryl Alcohol

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

Furfuryl triphenylmethyl ether, $C_4H_3O\text{-}CH_2\text{-}O\text{-}C(C_6H_5)_3$, was prepared and found to be a convenient derivative for the identification of furfuryl alcohol. Similarly, the furfuryl ether of 9,10-diphenyl-9,10-dihydroanthracenediol was studied.

Nine grams of triphenylchloromethane was added to a cold (0°) mixture of 3.3 g. of furfuryl alcohol and 40 cc. of pyridine. It was left for one and a half days at room temperature. Then it was diluted with 10 cc. of water and the resulting precipitate crystallized from alcohol. The white plates which formed melted at 137–139°; yield, 4 g.

Anal. Subs., 0.1892: CO_2, 0.5837; H_2O, 0.1041. Calcd. for $C_{24}H_{20}O_2$: C, 84.7; H, 5.92. Found: C, 84.2; H, 6.12.



Diphenyldihydroanthroanthracenediol was prepared by the method of Haller and Guyot[2] from phenylmagnesium bromide and anthraquinone. Then 4.4 g. of it was refluxed for one hour with 2.2 g. of furfuryl alcohol and 20 cc. of acetic anhydride.

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[1] Quaker Oats Fellow, 1929–1930.

[2] Haller and Guyot, *Compt. rend.*, 138, 327 (1904).

On cooling, needle crystals separated which, after recrystallization from alcohol, gave 0.5 g. of light cream-colored needles which melted at 223°. The analytical data were satisfactory for the monofurfuryl ether of the diol.

Anal. Subs, 0.1886: CO_2, 0.5763; H_2O, 0.0928. Calcd. for $C_{31}H_{24}O_3$: C, 83.8; H, 5.41. Found: C, 83.4; H, 5.47.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED AUGUST 8, 1932
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Note on the Preparation of Trialkyl Phosphates and their Use as Alkylating Agents

BY C. R. NOLLER AND G. R. DUTTON

Alkyl halides, sulfates, sulfites and sulfonates appear to be the best general alkylating agents known but because none of these classes of compounds is entirely satisfactory, it was considered desirable to investigate the use of other esters for this purpose. Preliminary experiments indicated that the alkyl borates, carbonates, nitrites and phosphites would be of no value, but the trialkyl phosphates showed some promise and were further investigated.

None of the various methods for preparing alkyl phosphates reported in the literature[1] proved as convenient as the reaction of phosphorus oxychloride with the alcohol in the presence of pyridine. This method is an adaptation of that used by Milobendski and Sachnovski[2] for the preparation of alkyl phosphites, in which benzene has been used as a solvent instead of ether and in which the pyridine hydrochloride is removed by adding water and removing the water layer instead of filtering off the solid pyridine hydrochloride.

In order to compare the various esters as alkylating agents a standard procedure was developed using one equivalent of alkylating agent per mole of phenol. This method was not devised for producing the maximum yield

TABLE I

YIELDS OF PHOSPHATES AND PHENOL ETHERS

	Phosphates		Phenol Ethers	
Ester	% Yield	B. p., °C.	% Yield	B. p., °C.
Ethyl sulfate	..	....	73.0	168–170
Ethyl phosphate	51.7	104–107 (16 mm.)	21.6	167–170
n-Propyl phosphate	63.5	128–134 (15 mm.)	Not run	
n-Butyl phosphate	74.0	160–162 (15 mm.)	39.0	204–211
Sec.-butyl phosphate	44.0	119–129 (8–12 mm.)	18.7	188–198
n-Amyl phosphate	63.7	158–163 (6 mm.)	15.0	125–128 (25 mm.)

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[1] (a) Evans, Davis and Jones, *J. Chem. Soc.*, 1310 (1930); (b) Bannister, U. S. Patent 1,799,349 (1931); (c) Johnson, British Patent 330,228 (1930).

[2] Milobendski and Sachnovski, *Chemik Polski*, 15, 34 (1917), [*Chem. Abs.*, 13, 2865 (1919)].

of ether but for ease of controlling conditions so that the results would be comparable. This accounts for the fact that the yield of phenetole using ethyl sulfate is not as high as that reported by Cade.[3] The yields of phosphates and phenol ethers are given in Table I.

It should be noted that while the yields of phenol ethers from phosphates are low compared with that from the sulfate, they are based on the amount of alkyl radical available. Many of the higher yields from other esters reported in the literature are based on the substance being alkylated, using a large excess of alkylating agent.

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[3] Cade, *Chem. Met. Eng.*, 29, 319 (1923).

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED AUGUST 30. 1932
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COMMUNICATIONS TO THE EDITOR

PREPARATION OF KETENE DIETHYL ACETAL

Sir:

According to the communication of Snell and McElvain [THIS JOURNAL, 55, **416** (1933)] these authors were unable to duplicate the preparation of ketene diethyl acetal described by me [Scheibler, Marhenkel and Nikolic, Ann., **458, 28** (1927)]. This preparation, however, has often been accomplished in my laboratory by several young chemists. The above failure may have been due to two causes. (1) The residue obtained from sodium ethoxide and ethyl acetate after removal of the volatile substances, containing the so-called "primary reaction product of the acetoacetic ester synthesis," may have lost alcohol during the treatment and been transformed into the sodium derivative of acetoacetic ester which, treated with water, of course did not give ketene acetal [Scheibler and Marhenkel, Ann., **458,** 6, 18 (1927)].

The evaporation of ether and the excess ester must be performed quickly at low temperature under diminished pressure. It is not surprising that Snell and McElvain, who dried the residue in a vacuum desiccator over sulfuric acid until it attained a constant weight, only obtained sodioacetoacetic ester. The weight of the dry residue obtained by them from **23** g. of sodium was only **90–100** g. instead of **125** g. A small amount of ethyl acetate may remain in the residue and be quickly saponified when it is treated with water, in contrast with ketene acetal, which does not undergo any decomposition in aqueous alkaline solution.

(2) The authors may have used too much calcium chloride in shaking the ether solution for three or four hours with three successive portions of powdered calcium chloride. I only employed a quantity just sufficient to fix the alcohol which was mixed with ketene acetal. When being shaken in this way ketene acetal is held by the great surplus of solid calcium chloride, which is not the case when a concentrated aqueous solution of calcium chloride is used. The separation of alcohol is better performed in such a manner. The directions given by me should be changed as follows.

After drying with anhydrous sodium sulfate, the ethereal solution from the extraction of the "primary reaction product" triturated with water, is distilled through a fractionating column. The residue containing ether only in a little amount is shaken intermittently during six hours with four parts of saturated aqueous solution of calcium chloride. Then it is extracted with ether in a continuous extraction apparatus and the resulting solution is dried with anhydrous sodium sulfate. Observing the precautionary measures mentioned before, ether and finally ketene acetal are distilled; yield, 13 g. or 11.2% of the calculated amount based on **23** g. of sodium used.

The preparation of dimethyl ketene diethyl acetal from ethyl isobutyrate was not successful with sodium ethoxide. It was performed in another manner which will be described later.

TECHNISCHE HOCHSCHULE OF BERLIN
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BERLIN-LICHTERFELDE, GERMANY
HELMUTH SCHEIBLER

RECEIVED OCTOBER 19, 1932 PUBLISHED JANUARY 11, 1933

KINETICS OF THE MERCURY SENSITIZED REACTION BETWEEN HYDROGEN AND OXYGEN

Sir:

Investigations of the mercury sensitized photo-reaction between hydrogen and oxygen have given rise to a large number of conflicting and unconnected data. These have been used to set up mutually conflicting theories of the mechanism of the reaction of hydrogen atoms with oxygen. It can, however, be demonstrated that almost all the known facts can be correlated and be completely in accord if we assume as the true mechanism:

$$\begin{array}{rll}
\mathrm{Hg} + h\nu & \longrightarrow \mathrm{Hg'} & I\ \mathrm{abs} \\
\mathrm{Hg'} + \mathrm{H_2} & \longrightarrow 2\mathrm{H} + \mathrm{Hg} & k_{\mathrm{H_2}} \\
\mathrm{Hg'} + \mathrm{O_2} & \longrightarrow \mathrm{O_2'} + \mathrm{Hg} & k_{\mathrm{O_2}} \\
\mathrm{H} + \mathrm{O_2} & \longrightarrow \mathrm{HO_2} & k_1 \\
\mathrm{HO_2} + \mathrm{H_2} & \longrightarrow \mathrm{H_2O_2} + \mathrm{H} & k_2 \\
\mathrm{HO_2} + \mathrm{HO_2} & \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} & k_3
\end{array}$$

These give the kinetic expression

$$\frac{d\,[\mathrm{H_2O_2}]}{dt} = \frac{k_2\,[\mathrm{H_2}]}{\sqrt{k_3}}\sqrt{\frac{[\mathrm{H_2}]\,k_{\mathrm{H_2}}\,I\ \mathrm{abs}}{[\mathrm{H_2}]\,k_{\mathrm{H_2}} + [\mathrm{O_2}]\,k_{\mathrm{O_2}}}} + \frac{[\mathrm{H_2}]\,k\mathrm{H_2}\ I\ \mathrm{abs}}{[\mathrm{H_2}]\,k_{\mathrm{H_2}} + [\mathrm{O_2}]\,k_{\mathrm{O_2}}}$$

Assuming $k_2/\sqrt{k_3} = 10^{-3}$, this equation fits exactly the data of Marshall [THIS JOURNAL, 49, 2763 (1927)] on the influence of $[H_2]$ and $[O_2]$ on the rate, if we put for k_{H_2} 1.1 X 10^7, k_{O_2} 0.68 X 10^7 as determined by Zemansky [*Phys. Rev.*, **36,** 919 (1930)]. The constant (Iabs) so obtained is constant to within less than 3% for all the experiments of Marshall not indicated as uncertain. Furthermore, the value of the quantum yield as calculated, using $k_2/\sqrt{k_3} = 10^{-3}$ lies between 1 and 2 in those experiments, in close agreement with those experimentally determined (1–2.5). In addition, the discrepancy between the quantum yield measurements of Frankenburger and Klinkhardt [*Z. physik.* Chem., **15B,** 421 (1931)] and by Marshall [*J. Phys. Chem.*, **30,** *1078* (1926); THIS JOURNAL, **54,** 4460 (1932)] is explained, in that the former used a light intensity a hundredfold greater than the latter. The mechanism postulated calls for a higher quantum yield with lower intensities, which is again in agreement with the experiments. This subject will be given a complete exposition in a paper shortly to be submitted to the JOURNAL.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
JOHN R. BATES

RECEIVED DECEMBER 5, 1932 PUBLISHED JANUARY 11, 1933

FURTHER REMARKS ON THE PREPARATION OF KETENE ACETAL

Sir:

Scheibler [THIS JOURNAL, **55,** 425 (1933)] ascribes our failure to obtain ketene acetal [*ibid.*, **55,** 416 (1933)], first, to too long standing of the "primary reaction product" over sulfuric acid, and second, to the use of excessive amounts of calcium chloride in the purification of the product. The first reason is not valid because we did not use a "primary reaction product" which had attained constant weight over sulfuric acid, but rather the residue left after the evaporation of the reaction mixture at room temperature under diminished pressure in a vacuum desiccator as described by the original investigators [Scheibler and co-workers, Ann., **458,** 28 (1927)]. On account of the second reason Scheibler now revises his original extraction procedure.

In consideration of this revised procedure we have made two further attempts to prepare ketene acetal. The same quantities of materials that were used in our earlier work were employed. The preparation of the "primary reaction product" was carried out in a tared 3-liter round-bottomed Pyrex flask. In this way it was possible to evaporate the ether and ethyl acetate from the reaction mixture and obtain a dry residue in about six hours, whereas evaporation in a vacuum desiccator according to the original procedure required about ten hours. It is not apparent to us how the time for this evaporation can be further decreased without the application of heat. The weight of the dry residue obtained in our latest experiments was in one case 77 g. and in the other 78 g. instead of 125 g. reported by the original investigators. In fact, intermittent weighing of the tared evaporation flask during the latter period of the evaporation showed that when its contents weighed 125 g. they were still liquid.

On working up these residues according to the revised procedure of Scheibler we obtained in one case 7 g. (A) and in the other 9 g. (B) of product at the point where ketene acetal should appear. In each of these products the amount of ethyl acetate was determined by saponification of an aliquot with 0.1 N potassium hydroxide and the amounts of ethyl alcohol and water were estimated by treatment of an aliquot with phenyl isocyanate followed by the isolation of the phenyl urethan and diphenyl urea. The following summary shows the percentages of these substances which were found to be present in the products which we obtained.

Product	Ethyl acetate, %	Alcohol, %[a]	Water. %	Total % found
A	13.0	72.5	2.2	87.7
B	0	87.5	1.5	89.0

[a] Analyses of a known mixture of alcohol and ethyl acetate, containing 85% of the former and 15% of the latter showed that only 85–90% of the alcohol could be recovered as the phenyl urethan, m. p. 52°.

These results show that the products which we obtained were mainly alcohol containing small amounts of water and ethyl acetate. It is our opinion that the failure of the found values to total 100% is due to the limitations of the procedure used for the determination of alcohol.

On the basis of our experiences, we believe that our failure to prepare ketene acetal is traceable to the discrepancy between the results reported by Scheibler and those obtained by us in connection with the formation of the so-called "primary reaction product" from ethyl acetate and sodium ethoxide. The results which we report now confirm our earlier conclusion that there is not only no evidence for, but definite evidence against, the existence of such a reaction product.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
JOHN M. SNELL
S. M. MCELVAIN

RECEIVED NOVEMBER 12, 1932 PUBLISHED JANUARY 11, 1933

BROMINE SENSITIZED PHOTO-DECOMPOSITION OF CHLORINE DIOXIDE

Sir:

Chlorine dioxide is decomposed by light with production of Cl_2O_6, light in the blue and ultraviolet being equally effective [Finkelnburg and Schumacher, *Z. physik.* Chem., Bodenstein Band, 704 (1931); Spinks, THIS JOURNAL, 54, 1689 (1932)]. Since the region of predissociation in

ClO_2 does not extend above **3750** Å., it was thought that further investigation would prove interesting. It is found that the quantum efficiency at **4360** Å. is only slightly less than that at **3650** Å. ClO_2 does not absorb at **5460** Å. and no photoreaction is obtained on isolating ClO_2 with light of this wave length using a mercury arc and glass filter. On adding a small percentage of bromine a sensitized photoreaction takes place using **5460** Å., the quantum efficiency being practically equal to that at **3650.** The equal efficiency of **3650** and 4360 Å. is explicable by the scheme suggested by Schumacher in which predissociation or the activation of ClO_2 molecules leads eventually to the production of 1ClO + $1ClO_3$ by one quantum of light. Apart from differences in energies of these groups one would expect any chains resulting to be of the same length. The equal quantum efficiency of **5460** Å. could be explained by

$$Br_2 + h\nu \longrightarrow Br_2'$$
$$Br_2' + ClO_2 \longrightarrow ClO_2' + Br_2$$

and then as before. It would be necessary that practically all the activated bromine molecules should be deactivated only by ClO_2 molecules under our conditions.

UNIVERSITY OF SASKATCHEWAN
SASKATOON, SASK., CANADA
J. W. T. SPINKS

RECEIVED DECEMBER 5, 1932 PUBLISHED JANUARY 11, 1933

ROTATORY DISPERSION IN THE VISIBLE AND THE ULTRAVIOLET RANGE OF CONFIGURATIONALLY CORRELATED CARBINOLS, HALIDES AND ACIDS

Sir:

High precision dispersion measurements in the visible and in the ultraviolet to about **2300** Å. have been made on the following substances, the configurations of which have been correlated by Levene and Marker.

Compounds	Sign of observed rotation in the visible	Sign of contribution of the functional group	Sign of contribution of the rest of the molecule
2-Methylbutanol	+	+	−
1-Bromide-2-methylbutane	−	+	−
1-Iodo-2-methylnonane	−	+	−
β-Methyl-*n*-valeric acid	−	+	−

It may be seen from this table that individual substances of this group vary in the direction of their rotation in the visible. An explanation of the differences in the direction of rotations of the correlated substances has been found by the analysis of their rotatory dispersion curves.

The dispersion curves of all these substances may be expressed by the two-term Drude formula

$$[M] = \frac{a}{\lambda^2 - \lambda_0^2} - \frac{a'}{\lambda^2 - \lambda_0'^2}$$

for rotatory dispersion. In our case the higher λ_0 value has a definite physical significance corresponding to a known absorption band (2050 Å. for COOH, 2560 Å. for I in 2-methyl-n-nonyl iodide). The contribution of the functional group (first term of above formula) is of opposite sign to the contribution of the rest of the molecule (second term). The direction of the first term is to the right and that of the second is to the left. It follows from this that in the levorotatory substances the sign of the contribution of the first band is opposite to the sign of the rotation of the substance observed in the visible. Thus, the sign of the rotation in the visible of the two halides is opposite to the sign of the contributions of Br and of I, which is contrary to the view expressed by W. Kuhn *[Ber.*, **63**, 191 (1930)], whereas in the secondary halides as well as in 1-bromo-3-methylpentane and in 1-iodo-4-methylhexane the direction of the contribution furnished by the halides determines the direction of the rotation in the visible.

The most striking example of the first band exerting a minor influence on the rotation in the visible is given by β-methyl-*n*-valeric acid. With decreasing wave lengths, the rotation increases slowly, reaches a maximum at 2850 Å., decreases sharply to a zero value at 2450 Å. and increases in the opposite direction for still smaller wave lengths. The molecular rotation in heptane is accurately represented (* 1%) by the equation

$$[M]^{25} = + \frac{8.088}{\lambda^2 - 0.042} - \frac{11.68}{\lambda^2 - 0.034}$$

The details of this study as well as the results dealing with the influence of the distance of the functional group on the sign of its contribution will be discussed in full in the near future.

THE ROCKERELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

P. A. LEVENE
ALEXANDRE ROTHEN

RECEIVED DECEMBER 7, 1932 PUBLISHED JANUARY 11, 1933

AN ABSOLUTE METHOD FOR ESTABLISHING ORIENTATION IN THE FURAN SERIES

Sir:

Identification of the simpler substitution products of furan, such as the methylated and halogenated furans, is not readily accomplished on account of the difficulty of obtaining solid derivatives from them. The observation that addition of maleic anhydride to furan and certain substituted furans[1] gives rise to crystalline solids, has led us to investigate this reaction as a general method for the identification of furan derivatives.[2] We have found that addition of maleic anhydride occurs with a variety of substituted

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(I) Diels and Alder, *Ber.*, 62, 554 (1929); Rinkes, Rec. *trav. chim.*, **50**, 1127 (1931).

(2) We are indebted to Professor Diels for his courtesy in permitting us to investigate this application of the maleic anhydride reaction.

furans but is hindered by the presence of certain substituents. Crystalline solids were obtained from 2-bromofuran (m. p. 116°), 3-bromofuran (m. p. 131.5–132°), furfuryl methyl ether (m. p. 97°), furfural diacetate (m. p. 126.5–127°), furfurylacetone (m. p. 86–87°) and several others. We have not succeeded in obtaining addition products from compounds containing a carbethoxyl, cyano, nitro or ethylenic group attached directly to the ring.

A study of the effect of hydrolytic agents upon the addition products (substituted 3,6-endoxo-A^4-tetrahydrophthalic anhydrides) has shown that they can be converted directly into the corresponding phthalic acids (or anhydrides).[3] Since the orientation of the substituents in the resulting phthalic acids (or anhydrides) is known, this transformation constitutes an absolute method for establishing the position of substituents in the furan ring. Thus, the substituted 3,6-endoxo-A^4-tetrahydrophthalic anhydrides from 2-methylfuran, 2- and 3-bromofuran on heating with hydrogen bromide in glacial acetic acid gave, respectively, 3-methylphthalic anhydride (m. p. 111–113°), 3-bromophthalic anhydride (m. p. 134–135°), and 4-bromophthalic anhydride (m. p. 108–110°). We are now engaged in extending the observations reported here.

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(3) Diels and Alder [Ann., 490, 243 (1931)] have shown that the addition product from furan and maleic acid can be converted into phthalic acid by a series of five reactions, involving four intermediate products.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, N. Y.

M. G. VAN CAMPEN, JR.
JOHN R. JOHNSON

RECEIVED DECEMBER 9, 1932 PUBLISHED JANUARY 11, 1933

VAPOR PRESSURE AND HEAT OF VAPORIZATION OF GRAPHITE

Sir:

A large amount of experimental work has been carried out in the past decade to determine the vapor pressure and heat of vaporization of graphite and very discordant values are given in the literature. We have recently investigated this problem, determining vapor pressure from the rate of loss in weight of carbon rings heated by high frequency induction in a vacuum [reported to April, 1932, Meeting, American Philosophical Society]. The interpretation of the results is complicated by the fact that carbon vapor exists in both monatomic and diatomic forms, the relative amounts being determined by the total pressure and the temperature. Vaughan and Kistiakowsky [*Phys. Rev.*, 40, 457 (1932)] have independently made calculations, using the equations of quantum statistical mechanics, which support this conclusion.

It is possible to reconcile our results in the temperature range 2350–2800°K. with those of Kohn and Gückel [*Z. Physik*, 27, 305 (1924)] on the vapor pressure of carbon in the arc.

They have taken the value of 4200°K. as the temperature of the positive crater at 1 atmosphere pressure. This value is due to Benedict [*Ann. Physik,* 49, 144 (1916)]. The method used by her has been adversely criticized by others and a careful search of the literature shows that this temperature may be 200° too high.

The following values are the heats of reaction for the two processes involved:

$$C_{\text{solid}} \longrightarrow C_{\text{monatomic vapor}} \qquad \Delta H = 177\ k.\ \text{cals.} \qquad (1)$$
$$C_2 \longrightarrow 2C \qquad AH = 150\ k.\ cals. \qquad (2)$$

The rate of loss in weight in g./sq. cm./sec. as a function of temperature is given by the formula

$$\log m = -\frac{177{,}000}{4.58T} + 2 \log T + \left(\frac{F^\circ - E_0^\circ}{4.58T}\right)_{\text{graphite}} + 3.174 \qquad (3)$$

This equation applies only to the carbon evaporating to form monatomic vapor. In the temperature range 2300–2800°K. this is 92–96% of the total carbon evaporating. The vapor pressure can be calculated from the rate of loss in weight by the equation

$$\log p = \log m + 1/2 \log T - 2.187 \qquad (4)$$

where p is expressed in atmospheres. The equation for the variation of the equilibrium constant of reaction (2) as a function of temperature is

$$\log \frac{(P_c)^2}{(PC\%)} = -\frac{150{,}000}{4.58T} + 3/2 \log T + \log (1 - e^{-2340/T}) + 1.462 \qquad (5)$$

When this equation is applied to the results of Kohn and Gückel the following values are calculated for the partial pressures of monatomic carbon vapor

T, °K.	Total pressure	P_c (atm.)	P_c (extrap.)
4200	1	0.21	0.17
4705	5	1.23	1.50

The fourth column gives the values extrapolated by equations (3) and (4) from the results in the temperature range 2350–2800°K. In making the extrapolation it was assumed that the latent heat of fusion of graphite was 8000 cal.

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y.
A. L. MARSHALL
FRANCIS J. NORTON

RECEIVED DECEMBER 9, 1932 PUBLISHED JANUARY 11, 1933

A SIMPLE TEST FOR STREAMING IN THE POROUS DIAPHRAGM DIFFUSION CELL

Sir:

The diffusion cell of Northrop and Anson [J. Gen. *Physiol.,* **12,** 543 1929)] as further standardized by McBain and Liu [THIS JOURNAL, 53, 59 (1931); see also M. E. Laing McBain, THIS JOURNAL, in press (1933)] is now widely used in this country and abroad as a highly convenient and accurate method. These authors eliminated bulk streaming of liquid through the sintered glass or other porous membrane by careful leveling of the membrane which separates the denser liquid above from the lighter liquid beneath. Several workers have obtained erratic results when using membranes that were too coarse.

We find that it is simplest to test all cells for streaming by using them once tilted at an angle such as 30°. If the pores are too coarse, the values for diffusion may be increased as much as four-fold as compared with either the same cell used horizontally or with a cell of fine pores. Such cells should be discarded because those with finer pores such as glass sintered membranes "G3" (2–5 × 10^4 Å) are scarcely affected by tilting.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIF.
C. R. DAWSON

RECEIVED DECEMBER 14, 1932 PUBLISHED JANUARY 11, 1933

THE RADIOACTIVITY OF LANTHANUM, NEODYMIUM AND SAMARIUM

Sir:

In view of the note in *Nature* 1130, 846 (1932)] by Hevesy and Pahl regarding the radioactivity of samarium, we wish to report an independent investigation on this subject. In October of this year we discovered radioactivity in a sample of samarium and since that date we have examined samples of lanthanum and neodymium which are also radioactive.

The method employs the Geiger–Miiller counter set-up as described by Libby [Phys. *Rev.,* 42, 440 (1932)]. The salts investigated have been deposited as a thin film on the inside of a glass tube. This is placed around the counter which is in the form of a long wire enclosed in a metal screen cylinder. In a typical run 20 g. of potassium chloride deposited on the tube increased the zero count of 15 per minute to 160.

The activities of the samples of lanthanum and neodymium are not appreciably screened by 0.07 mm. of aluminum, whereas that of samarium is very largely, if not completely, screened, indicating that the activities of the former are mainly of the beta type and that of the latter alpha. We have used two different samples of neodymium, one sulfate and the other oxalate. Both show an activity which is approximately 2.5 times that of potassium per mole. The lanthanum activity per mole is about 8 times that of potassium and the samarium approximately **3** times. A careful examination of a very pure sample of gadolinium sulfate prepared by Professor B. S. Hopkins gave results which are negative to at least 2% per mole of the activity of potassium.

We believe that the radioactivity of these elements is due to the presence of unstable isotopes, but have not completely eliminated the possibility of actinium as an impurity in the lanthanum and neodymium samples. This point is under investigation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

W. F. LIBBY
W. M. LATIMER

RECEIVED DECEMBER 27, 1932 PUBLISHED JANUARY 11, 1933

NEW BOOKS

A History of Chemistry. By F. J. MOORE, **Ph.D.,** Late Professor of Chemistry in the Massachusetts Institute of Technology. Second edition. Revision prepared by William T. Hall. McGraw-Hill Book Company, Inc., **370** Seventh Ave., New York, **1931.** **xxiii + 324** pp. Illustrated. **14.5 × 21** cm. Price, **$3.00.**

The revision of this serviceable book has not involved a departure from the general plan of the first edition. The essential change, apart from restatements necessitated by recent discoveries, is the inclusion of biographical sketches of two groups of chemists, *viz.*, (1) brilliant chemists who died during the last twelve years and (2) deceased American chemists who contributed material to the development of chemistry in this country. It is to be regretted that the bibliography at the end of the chapters has not been enlarged, particularly since so many admirable articles on the history of chemistry have appeared during the last ten years in the ***Journal of Chemical Education.*** The chapter devoted to chemistry in the United States would be more in harmony with the rest of the book, and certainly more useful to American students, if the growth was described as a connected narrative rather than in the form of disconnected biographies. However, the book as revised is an excellent example of books in its field and a faithful expression of the scholarship of the author, whose life as a scientist and as a teacher is briefly recounted in the introductory portion.

LYMAN C. NEWELL

Elementary Qualitative Analysis for College Students. By J. H. **REEDY,** Associate Professor of Chemistry in the University of Illinois. Second edition. The McGraw-Hill Book Co., Inc., **330** West 42d St., New York, **1932.** **x + 163** pp. **13** figs. **14** X **21** cm. Price, **$1.50.**

"The changes consist mainly in the inclusion of new procedures based upon reagents recently developed, and the extension of older methods to more difficult combinations.... Practically the whole book has been rewritten.... If the book has a distinctive feature, it is the emphasis placed upon interpretative work on the part of the student."

Preliminary experiments, notes, and exercises following each group will convince the student that the reagents and conditions as specified are well planned to separate the ions sharply and to detect them with certainty.

The theoretical treatment is clear and helpful. Greater stress might have been laid upon the fact that the whole of qualitative analysis can be formulated in terms of a very limited number of equilibria, and displacements of the same.

Here and there are statements which could be revised to advantage, and without appearance of pedantry. Thus ionic precipitates (p. 2) appear to be produced from insoluble molecules preexisting in solution. Stannic chloride and even stannic ion (p. **25)** are pictured as stable in water. "NH_4OH is a very weak base" (p. **81).** The electromotive series (p. **151)** is merely a column of metals, rather than a comprehensive system of oxidizing and reducing agents arranged in pairs, the order of which depends upon concentrations.

This book is highly teachable. Grounds for criticism are few indeed, and unimportant when contrasted with its many admirable qualities.

G. S. FORBES

Lehrbuch der **Metallkunde. Chemie und** Physik der Metalle und ihrer Legierungen. (Textbook of **Metals.** Chemistry and Physics of Metals and their Alloys.) By GUSTAV **TAMMANN,** Gottingen. Fourth, enlarged edition. **Verlag** von **Leopold** Voss, **Salomonstrasse 18** B, **Leipzig C** 1, Germany, **1932.** xv + *536* pp. **385** figs. **15.5** X **23.5** cm. Price, **RM. 48;** bound, RM **49.50.**

This is the fourth edition of Tammann's well-known work, the first three of which, in **1914, 1921** and **1923** were issued under the title Lehrbuch der Metallographie. The former title connotes a study of the microscopic structure of metals, and since this book covers much more, the title is very properly changed to be more descriptive of the contents. As compared with the last edition, there has been a 50% increase in the number of diagrams, and a somewhat smaller increase in the number of pages and new text. The new text covers both new methods which have come into prominence during the last ten years, such as a description of the work of the German metallurgists on the plastic deformation of single crystals and a more adequate description of x-ray methods of analysis, and also the vast amount of new experimental knowledge of the phase diagrams of alloys. The old text has also in many cases been revised, but not in all. Thus, the very first sentence of the introduction is the same as the introduction of the original **1914** edition: "By the word alloy was understood, **30** or 40 years ago. . . ."

As is perhaps natural for an author who has himself covered so many of the fields of activity of the metallurgist, the emphasis is perhaps too much on Tammann's personal activities to give a well-balanced presentation of the whole subject. Thus it is unfortunate that matters in which Tammann does not agree with other investigators are presented without a reference to the other side or even an intimation that there is difference of opinion, such as the course of the melting curve at high pressures, and the significance of the behavior of eutectic and other mixtures under acid attack. There is also too little tendency to mention work in other countries than Germany. For instance, the important work of Hume-Rothery on intermetallic compounds is not mentioned by name, and in the tables the old formula Ag_2Zn_3 is retained instead of the new Ag_5Zn_8, which is the basis of part of Hume-Rothery's theory, although there is in the text a brief reference to Ag_5Zn_8 in terms which cannot possibly bear on the Ag_2Zn_3 of the table.

When due allowance is made for all defects, however, the book remains a monumental one, and a record of an almost incredible amount of achievement for which Tammann has been personally responsible. No one can read it without being stimulated by the extraordinary range and vivacity of Tammann's imagination. What other author could present us from his personal experience with an array of topics, all of them made to have suggestive implications, such as: "The dependence of nuclear number on subcooling," "The spreading of mercury drops on metallic surfaces," "The precipitation of polonium from its solutions," "Change of color on cold-working," "The change with temperature of the angle at which two polished plates slide on each other," to mention only a few?

P. W. BRIDGMAN

Die experimentellen und theoretischen Grundlagen der Elektronenbeugung. (The Experimental and Theoretical Principles of Electron Diffraction.) By H. MARK and R. WIERL. Verlagsbuchhandlung Gebrüder Borntraeger, Schöneberger Ufer 12a, Berlin W 35, Germany, 1931. iii + 126 pp. 60 figs. 16.5 × 25 cm. Price, to subscribers, unbound, RM. 12; bound, RM. 13.60. Separately, unbound, RM. 16; bound, RM. 18.

What impresses one most about this monograph of Mark and Wierl is its completeness—no paper on the diffraction of electrons by atoms, molecules or crystals, either theoretical or experimental, has eluded the authors' attention, and none has failed to supply illumination to their text. In 126 pages the content of some 150 articles which constitute the literature of their subject up to April, 1931, is organized and reviewed in a discriminating and pleasing manner. This is particularly true of the sections devoted to the experimental work, which together make up about three-fourths of the whole.

The contributions which the authors have themselves made in this field are well known—particularly their important and beautiful work on the diffraction of electrons by molecular vapors. It is not surprising perhaps that with their interests more deeply engaged on the experimental side, their treatment of this part of the subject strikes one as rather more sure-footed than their treatment of the purely theoretical part. The latter is marred unfortunately by numerous typographical errors not all of which are corrected by a table of errata. With this not very important reservation, the monograph may be recommended as a comprehensive survey of its subject and a reliable guide to the literature.

The death of the junior author, announced recently in German periodicals, has come as a shock to physicists the world over. It would be difficult indeed to think of a young experimental physicist who had shown greater promise than Dr. Wierl.

C. J. DAVISSON

Manuale di Analisi Chiiica. Clinica, Fisio-patologica ed Igienica ad Uso dei Medici e Studenti. (Manual of Chemical Analysis: Clinical, Physio-Pathological and Hygienic. For the Use of Physicians and Students.) By CESARE SERONO and ALFONSO CRUTO. Second edition. Unione Tipografico-Editrice Torinese, Torino, Italy, 1932. xv + 483 pp. 85 figs. 15 × 22.3 cm.

This is an elementary textbook of the kind used by medical students thirty years ago, except that many of the biochemical methods described are fairly modern. It deals more exclusively with ordinary qualitative and quantitative analysis than with the analysis of biological material and does not correspond very closely to biochemistry as it is taught in this country.

OTTO FOLIN

Wissenschaftliche Photographie. Eine Einführung in Theorie und Praxis. (Scientific Photography. An Introduction to Theory and Practice.) By Dr. E. v. ANGERER, Professor at the Technical High School of Munich. Akademische Verlagsgesellschaft m. b. H., Leipzig C 1, Germany, 1931. viii + 185 pp. 99 figs. 16 × 24 cm. Price, M. 11, unbound; M. 12.80, bound.

This book fills in the gap between the elementary practical handbooks of photography on the one hand, and the very comprehensive treatises on the other. It provides a good general survey of the most important aspects of practical and theoretical photography, in terms familiar to the physicist and chemist, and in a manner calculated to assist them in an intelligent understanding of the principles of the science which they employ in a considerable part of their work. It is regrettable that the average scientific worker is unable to make the best of use of the photographic process, owing to an incomplete understanding of the properties, and limitations, of photographic materials, and of the elementary principles underlying the photographic process. A study of this book should be of considerable help to him wherever he applies photography to his scientific or technical work.

WALTER CLARK

Les Problêmes de la Biochimie Moderne. (Problems of Modern Biochemistry.) By G. FLORENCE, Professor in the Faculty of Medicine of the University of Lyon, and J. ENSELME, Docteur ès Sciences, Faculty of Medicine, Lyon. Preface by L. Hugounenq. G. Doin et Cie, Éditeurs, 8, Place de l'Odéon, Paris 6^e, France, **1932. 312** pp. Illustrated. **15** X **24.5** cm. Price, fr. **45.**

Reading the table of contents of this book impresses one with its excellent plan. The first half is devoted to a description of biochemical molecules--static biochemistry. The second half includes a section on kinetic biochemistry and another on physiological chemistry. There is an appendix on nomenclature and another on thermodynamics.

The execution of the plan, however, is less satisfactory. Most useful publications relating to biochemistry are textbooks, monographs or accounts of investigations. In writing this book the authors have fallen between two stools; the result is less complete than a textbook and less precise and up-to-date than a monograph. Chapters **5–7** on the amino acids, peptides and proteins illustrate the point. These chapters contain less than one finds in many textbooks. Since the **52** literature references include only **3** which are later than **1927** the treatment is hardly more up-to-date than Cohn's "Physical Chemistry of the Proteins" published in ***Physiological Reviews*** seven years ago.

The numerous typographical errors are irritating and sometimes bewildering. The **24** items listed in the "Errata" are but a small proportion of the errors which occur. Thus on p. **192** one finds $[\bar{O}]$ for [OH], **(H^2)** for $[\overset{+}{H}]^2$ and on p. 197, 6 **1** for **6.1.** One receives the impression that the chances are against correct spelling of English words. There are **4** English titles in the bibliography of Chapter II and a word is misspelled in each, *viz.*, *colloïdal, proteines, leathe, dynamies*. An amusing aspect of the carelessness in proof reading is the originality in abbreviation. At least ten different abbreviations for *Zeitschrift* may be found.

D. B. DILL

Quantitative Clinical Chemistry. Volume II. Methods. By JOHN P. PETERS, M.D.. M.A., Professor of Internal Medicine, Yale University School of Medicine, and DONALD D. VAN SLYKE, Ph.D., Sc.D., Member of the Rockefeller Institute for Medical Research. The Williams and Wilkins Company, Mt Royal and Guilford Aves., Baltimore, Md., **1932.** xix + **957** pp. Illustrated. **15.5** X **23.5** cm. Price. **$10.00.**

This long expected volume has now appeared and it is doubtless being examined by many who knew beforehand that they must own it. Like the first volume, it is primarily a book for clinicians rather than for chemists. Its **32** chapters cover about every kind of quantitative measurement and determination called for in completely equipped clinical laboratories. But the book is not a compendium or handbook giving a description of all of the better known methods. The 200-page section devoted to the description of gasometric methods is by far the most comprehensive and complete and naturally so because of Van Slyke's extensive work in this field of analysis. Many of the other chapters are unexpectedly brief. In these chapters, the authors, as is explained in the preface, have endeavored to confine themselves to the description of one method representing each of the major fundamental principles of analytical chemistry, such as weighing, titration and colorimetry.

This scheme, excellent as it may be in the field of inorganic analysis, does not correspond very well to the development of biochemical analysis during the past twenty years, and the authors have not been able to adhere to it with any high degree of uniformity. The plan has also compelled the authors to assume the responsibility of selecting one out of several methods of sometimes equal and in other cases of unequal merit. In the case of uric acid in urine, for example, nearly all present-day determinations are made colorimetrically, and several reliable procedures based on this principle are known. Only one colorimetric method is given for this determination, however, and it happens to be a short-cut method which is unreliable in practice and theoretically indefensible. The extensive experience of the authors has of course saved them from making many such unfortunate selections. Most of the methods selected for description are undoubtedly capable of yielding valid results even though, in some cases, they are not the best known or most widely employed. Among the methods of doubtful validity should perhaps be cited those given in Chapter 19 on the determination of phenols in blood and in urine. This statement is in no sense a reflection on the authors, but it is probably a fact that the methods as yet available for the determination of phenols, including the methods for which the reviewer is responsible, should still be regarded only as tentative or provisional procedures.

Chapter 15 is rather interesting in that here the authors describe the method for the determination of creatinine in blood and admit that they still use the method while at the same time they endorse the view that blood contains no creatinine. That view rests on rather slender evidence, but the interpretation is important since it carries with it the corollary, also accepted by the authors, that the creatinine in the urine is formed in the kidneys.

Most of the chapters in the book open with a general discussion more or less historical in character, and all of the different chapters contain a generous supply of references to original literature. Some of the described methods are based only on personal communications.

The appearance of this book has one especial significance. As its title indicates, it deals only with quantitative determinations. The innumerable often meaningless and sometimes misleading qualitative tests, which still represent nearly all that many clinicians know about the applications of biochemistry, are omitted. Teachers of biochemistry in medical schools might well note the important hint implied in the appearance of such a book by two such eminent authors.

OTTO FOLIN

Chemistry of the Opium Alkaloids. By LYNDON F. SMALL. Consultant in Alkaloid Chemistry, United States Public Health Service, and ROBERT E. LUTZ, Associate Professor of Chemistry, University of Virginia. Prepared by direction of the Surgeon-General as Supplement No. 103 to the Public Health Reports. Superintendent of Documents, Government Printing Office, Washington, D. C. ix + 375 pp. 15.5 X 23.5 cm.

Seldom, in all probability, has such a wealth of detailed information in reasoned form been presented in so small a compass as in this volume, which is a result of co-operative work between the Committee on Drug Addiction of the Division of Medical Sciences of the National Research Council and the Division of Mental Hygiene of the U. S. Public Health Service. Those who have followed the painstaking investigations in the domain of alkaloid chemistry published from the laboratory of the authors must have recognized the erudition which had necessarily to be acquired before research in this intricate and well-explored field could be undertaken, That the fruit of so much laborious reading has now been laid before the public, in palatable and relatively assimilable form, is truly a matter for congratulation.

The subject matter is divided into two parts, dealing with the alkaloids derived, respectively, from benzylisoquinoline and from phenanthrene; each part is subdivided into about eighteen sections devoted to individual alkaloids and their immediate derivatives. Every section is constructed on the general plan: (1) history, (2) empirical description, (3) development of constitution, (4) synthesis, (5) description of salts and derivatives, (6) bibliography. Not a word is wasted, nor is, apparently, a pertinent fact omitted. By means of an appendix, covering the literature of about two years, the information has been brought up to date of January 1,1932.

Professor Wieland, in an appreciative Foreword, subscribes to the belief of the authors that "every reaction and every compound described in the literature is mentioned," and points out that this book far transcends a mere systematic collection of facts by virtue of its historical and critical treatment of the questions of constitution. Organic chemists should be grateful to the authors and to the government for publishing so impressive and valuable a work.

H. T. CLARKE

BOOKS RECEIVED

November 15, 1932–December 15, 1932

GEORGE L. CLARK. "Applied X-Rays." Second edition. McGraw-Hill Book Company, Inc., 330 West 42d St., New York. 470 pp. $5.00.

JEAN-LOUIS DESTOUCHES. "État Actuel de la Théorie du Neutrons." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris Ve, France. 68 pp. Fr. 18.

L. W. EASTWOOD. "Introduction to Metallography." Mimeographed edition. Edwards Brothers, Inc., Lithoprinters and Publishers, Ann Arbor, Mich. 137 pp.

J. FRENKEL. "Wave Mechanics. Elementary Theory." Oxford University Press, 114 Fifth Ave., New York. 278 pp. $5.00.

STEFAN GOLDSCHMIDT. "Stereochemie." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 311 pp. M. 27.80; bound, M. 29.

G. ALBERT HILL AND LOUISE KELLEY. "Organic Chemistry." P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa. 564 pp. $3.00.

DAVID INGERSOLL HITCRCOCK. "Physical Chemistry for Students of Biology and Medicine." Charles C. Thomas, Publisher, 220 East Monroe St., Springfield, Illinois. 182 pp. $2.75.

MURRAY P. HORWOOD. "The Sanitation of Water Supplies." Charles C. Thomas, Publisher, 220 East Monroe St., Springfield, Illinois. 181 pp.

J. W. MELLOR. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XII. Uranium, Manganese, Masurium, Rhenium, Iron." Longmans, Green and Co., 55 Fifth Ave., New York. 944 pp. $20.00.

PRAFULLA CHANDRA RÂY. "Life and Experiences of a Bengali Chemist." Chuckerverty, Chatterjee and Co., Ltd., Booksellers and Publishers, 15 College Square, Calcutta, India. 557 pp.

SALOMON ROSENBLUM. "Origine des Rayons Gamma. Structure Fine du Spectre Magnétique des Rayons Alpha." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris Ve, France. 37 pp.

LUDWIG SCHMITT. "Der Einfluss der Handelsdunger auf das Pflanzenwachstum und auf verschiedene Eigenschaften kalkarmer Mineralboden." Verlagsgesellschaft für Ackerbau m. b. H., Dessauer Strasse 31, Berlin SW 11, Germany. 186 pp. RM. 9.

W. STRECKER. "Qualitative Analyse auf praparativer Grundlage." Third edition. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 10, Germany. 203 pp. RM. 8.

BRUNO WAESER. "Die Luftstickstoff-Industrie mit Berücksichtigung der chilenischen Industrie und des Kokereistickstoffs." Second, revised edition. Verlag von Otto Spamer, Heinrichstrasse 9, Leipzig C 1, Germany. 509 pp. Rmk. 30; bound, Rmk. 33.

RICHARD WILLSTÄTTER. "Hundert Jahre Liebigs Annalen der Chemie." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 12 pp.

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 55 FEBRUARY, 1933 NUMBER 2

Third Report of the Committee on Atomic Weights of the International Union of Chemistry

BY G. P. BAXTER (Chairman), MME. M. CURIE, O. HÖNIGSCHMID, P. LE BEAU AND R. J. MEYER

The following report of the Committee covers the twelve month period, September 30, 1931 to September 30, 1932.[1]

Only two changes in the table of atomic weights are recommended, from 126.932 to 126.92 in the case of iodine and from 138.90 to 138.92 in the case of lanthanum.

Physico-chemical Methods

Carbon.—Moles and Salazar[2] have determined the normal density of carbon monoxide prepared by four methods: (1) reaction of sodium formate with phosphorus pentoxide, (2) dehydration of formic acid with phosphoric acid, (3) dehydration of formic acid with concentrated sulfuric acid, (4) reaction of potassium ferrocyanide with concentrated sulfuric acid. In each case the gas was subjected to chemical purification and then was fractionally distilled.

THE DENSITY OF CARBON MONOXIDE

Preliminary Series

Method	Globe N-2 608.87 ml.	Globe G 987.52 ml.	Average
1	1.25058	1.25006	1.25032
2	1.25076	1.24984	1.25030
	1.25013	1.24986	1.24999
	1.25130	1.25018	1.25074
	1.25105	1.25024	1.25064
	1.25073	1.25027	1.25050
	(1.25124)	(1.25081)	(1.25102)
	1.25095	1.25090	1.25092
	1.25019	1.24945	1.24982
Average	1.25073	1.25011	1.25042

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(1) Authors of papers bearing on the subject are requested to send copies to each of the five members of the Committee at the earliest possible moment: Prof. G P. Baxter, Coolidge Laboratory, Harvard University, Cambridge, Mass., U. S A ; Mme. Prof. M. Curie, Institut du Radium, 1 Rue Pierre Curie, Paris Ve, France; Prof. O. Honigschmid, Sofienstrasse 9/2, Munich, Germany; Prof. P Le Beau, Faculté de Pharmacie, 4 Avenue de l'Observatoire, Paris VIe, France; Prof. R. J Meyer, Landshuter Str. 11-12, Berlin W 30, Germany.

(2) Moles and Salazar, *Anales soc. españ. fís. quím.*, **30**, 182 (1932)

THE DENSITY OF CARBON MONOXIDE *(Concluded)*

Final Series

Method	Globe N 992.04 ml.	Globe G 987.62 ml.	Average
2	1.24953	1.24980	1.24966
	1.25000	1.25053	1.25026
	1.24941	1.24992	1.24966
	1.24953	1.25046	1.24999
Average	1.24962	1.25018	1.24989
3	1.24920	1 24951)	1.24939
	1.24972	1.25039	1.25005
	1 25179	1.25067	1.25123
	1 25003	1.25109	1.25056
	1.25061	1.24997	1.25029
	1.24930	1.25019	1.24974
	1.25029	1.24973	1.25001
Average	1.25013	1.25023	1.25018
4	1.24966	1.25056	1.25011
	1.24968	1.25105	1.25036
Average	1.24967	1.25081	1.25023
Average of all	1,24990	1.25030	1.25010

This result is in exact agreement with that previously found by Pire and Moles. With the values 22.414 and 1.00050 for R and 1 + λ, respectively, the atomic weight of carbon is calculated to be 12.006. Because of the small coefficient of deviations from Boyle's law, carbon monoxide is as well suited for precise molecular weight determination as the permanent gases, so that this result may be accepted as a valuable addition to the evidence which has been accumulating recently that the atomic weight of carbon is somewhat higher than 12.00.

Nitrogen.—Batuecas[3] has continued the investigation on nitrous oxide, previously reported, by determination of the density at pressures below one atmosphere. The gas was prepared (1) by the reaction of hydroxylamine hydrochloride and sodium nitrite, (2) by the decomposition of ammonium nitrate. Chemical purification was followed by condensation and fractional distillation. The values given in the following table are

THE DENSITY OF NITROUS OXIDE

P = 506.67 mm.

Method	Globe G 1007.56 ml.	Globe N-3 772.58 ml.	Average
1	1.9749	1.9741	1.9745
1	1.9750	1.9744	1.9747
1	1.9743	1.9746	1.9745
Average	1.9747	1.9744	1.9746
2	1.9744	1.9744	1.9744
2	1.9738	1.9745	1.9741
2	1.9745	1.9758	1.9751
Average	1.9742	1.9749	1.9745

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(3) Ratuecas. J. chim. *phys.*, **28**, 572 (1931); *Anales soc. españ. fís. quím.*, *89*, 538 (1931).

THE DENSITY OF NITROUS OXIDE *(Concluded)*

Method	Globe G 1007.55 ml.	Globe N-3 772.58 ml.	Average
	$P = 380$ mm.		
1	1.9723	1.9721	1.9722
1		1.9719	1.9719
1		1.9706	1.9706
1	1.9724	1.9724	1.9724
Average	1.9724	1.9718	1.9718
2	1.9718	1.9719	1.9718
2	1.9726	1.9730	1.9728
2	1.9722	1.9730	1.9726
Average	1.9722	1.9726	1.9724
	$P = 253.33$ mm.		
1	1.9695	1.9701	1.9698
1	1.9685	1.9700	1.9692
1		1.9677	1.9677
1	1.9691	1.9691	1.9691
Average	1.9690	1.9692	1.9690
2	1.9701	1.9698	1.9700
2	1.9691	1.9701	1.9696
2		1.9700	1.9700
Average	1.9696	1.9700	1.9699

referred to one atmosphere without correction for the deviation from Boyle's law.

The limiting density is calculated on the assumption that a linear relation holds between pressure and density referred to one atmosphere.

Pressure, atmospheres	Density	Limiting density	$1 + \lambda$
1	1.9804		
$^2/_3$	1.9746	1.9630	1.00886
$^1/_2$	1.9722	1.9640	1.00835
$^1/_4$	1.9694	1.9639	1.00840
	Average	1.9636	1.00854

The calculation of $1 + \lambda$ by linear extrapolation of values for PV found from the expression $L_1/L_P \frac{P_1}{P}$ gave the following result

Pressure. atmospheres	PV	$1 + \lambda$
I	1,00000	
$^2/_3$	1.00294	1.00882
$^1/_2$	1.00416	1.00832
$^1/_3$	1.00559	1.00839
	Average	1.00851

With the values 1.9804, 22.414 and 1.0085 for the density at one atmosphere, R and $1 + \lambda$, respectively, the molecular weight of nitrous oxide is found to be 44.014 and the atomic weight of nitrogen 14.007.

In an article devoted chiefly to criticism of the report of this Committee for 1931, Moles(4) applies corrections to the above results (1) for diminution in volume of the globes when filled at low pressures and (2) for adsorption as found by Crespi in work as yet unpublished. The corrected figures are as follows

Pressure atmospheres	Density	Limiting density	$1 + \lambda$	N_2O
1	1.98034			
$^2/_3$	1.97459	1.96309	1.00880	44.001
$^1/_2$	1.97223	1.96412	1.00829	44.023
$^1/_3$	1.96946	1.96402	1.00833	44.022
Average		1.96364	1.00845	44.016

Whence N = 14.008

Fluorine.—Moles(5) discusses critically earlier determinations of the atomic weight of fluorine with the final conclusion that the atomic weight of this element is very close to integral, 19.000, and suggests that the higher value recently found by Patterson, Whytlaw-Gray and Cawood, through the density of methyl fluoride, is due to the effect of impurity of methane in the methyl fluoride employed by the latter. Patterson, Whytlaw-Gray and Cawood(6) have prepared methyl fluoride by their own (Collie's) method (pyrolysis of tetramethylammonium fluoride) and that of Moles and Batuecas (action of potassium methyl sulfate on potassium fluoride) and found that the two samples had identical critical constants within the error of the experiments. A direct determination of the compressibility of methyl fluoride yielded the values 1.0114 at 0° and 1.0087 at 21°. The latter is essentially identical with the value calculated from their experiments with the micro-displacement-balance but the former is much lower than that found by Moles and Batuecas from gas density measurements, 1.018. Batuecas(7) discusses the calculation of Patterson, Whytlaw-Gray and Cawood's density determinations with the micro-balance and points out that since the methyl fluoride employed by Moles and Batuecas possessed a vapor pressure obeying the law $\log p = -(A/T) + B$ it must have been essentially free from impurity. The Committee feel that the preponderance of evidence is in favor of the lower value for fluorine and see no reason at present to alter the value in current use.

Potassium.—Heller and Wagner(8) were unable to detect by analysis of potassium chloride from plant sources any concentration of the higher isotope of potassium. This confirms their previous finding.(9)

Selenium.—Hönigschmid(10) has synthesized silver selenide from pure silver and pure selenium. The product was brought to constant weight in

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(4) Moles, *Anales soc. españ. fís. quim.*, 80, 460 (1932).
(5) Moles, *J. chim. phys.*, 29, 53 (1932); *Nature*, 128, 966 (1931).
(6) Patterson, Whytlaw-Gray and Cawood, *ibid.*, 129, 245 (1932); *J. Chem. Soc.*, 2180 (1932).
(7) Batuecas, *J. chim. phys.*, 29, 269 (1932).
(8) Heller and Wagner, *Z. anorg. allgem. Chem.*, 206, 152 (1932).
(9) Heller and Wagner, *ibid.*, 200, 105 (1931).
(10) Hönigschmid, *Naturwiss.*, 20, 659 (1932).

vacuum. Eleven experiments yielded the ratio 2Ag : Ag_2Se = 0.732081 and the atomic weight of selenium 78.962. This value agrees with Aston's value and is considerably lower than the current one. Until further details are available no change is recommended in the table.

Iodine.—Hönigschmid and Striebel[11] have continued their experiments on the conversion of silver iodide to silver chloride, with precipitated silver iodide, instead of material synthesized from the elements used previously.

Iodine was three times distilled from iodide solutions prepared from similar iodine and was sublimed in an oxygen current over red hot platinum. From this iodine hydriodic acid was prepared by direct synthesis with hydrogen and after solution in water this acid was distilled.

Sample A of silver iodide was precipitated by adding an excess of 0.15 N hydriodic acid solution to an acid solution of the purest silver (0.15 N). Sample B was precipitated in ammoniacal solution and then an excess of nitric acid was added. Sample C was prepared by adding 0.2 *N* ammoniacal silver nitrate to an excess of 0.2 N ammoniacal ammonium iodide. Sample D resulted from adding an excess of 0.16 *N* silver nitrate to 0.16 N hydriodic acid.

After washing and drying the silver iodide was fused in an air current containing free iodine and then in pure air in a weighed quartz tube, and weighed. Then the silver iodide was converted to silver chloride by heating in a chlorine current at gradually increasing temperatures up to fusion. Proof was secured that the iodide did not retain iodine and that the conversion was complete. Vacuum weights are given.

THE ATOMIC WEIGHT OF IODINE

Sample	Wt. of AgI	Wt of AgCl	Ratio AgI:AgCl	At. wt., I
A	14.41889	8.80228	1.638085	126.918
A	10.61180	6.47828	1.638058	126.914
A	13.61047	8.30885	1.638070	126.916
B	17.91554	10.93678	1.638100	126.920
A	14.11519	8.61692	1.638078	126.917
A	14.03900	8.57050	1.638061	126.915
A	13.39032	8.17448	1.638064	126.915
B	11.47497	7.00511	1.638085	126.918
B	13.49506	8.23839	1.638070	126.916
B	14.36421	8.76879	1.638106	126.921
C	10.72744	6.54879	1.638080	126.917
C	8.42456	5.14298	1.638069	126.916
D	14.91865	9.10741	1.638078	126.917
D	12.57197	7.67526	1.638050	126.918
D	8.28549	5.05809	1.638067	126.916
C	13.95958	8.52190	1.638083	126.918
C	9.21692	5.62671	1.638066	126.916
		Average	1.638076	126.917

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(11) Hönigschmid and Striebel, *Z. anorg. allgem. Chem.*, **208**, 53 (1932).

In view of the concordance of this result and the earlier one of Hönigschmid and Striebel (see report for 1931) the atomic weight of iodine is changed in the table from 126.932 to 126.92.

Tellurium.—Hönigschmid[12] has prepared and analyzed tellurium tetrabromide. From the two ratios $TeBr_4 : 4Ag$ and $TeBr_4 : 4AgBr$ the atomic weight of tellurium is found to be 127.587.

Krypton and Xenon.—Allen and Moore[13] have separated krypton and xenon from liquid air residues by means of fractional distillation. The average density of the purest krypton fractions, found with a globe of 22 ml. capacity, was 3.733 and that of the purest xenon 5.887. Using values calculated by Watson in 1910 for the compressibilities of these gases the atomic weights of krypton and xenon are found to be 83.6 and 131.4 with an uncertainty of 0.1 unit in each case. These results, which agree with the recent results of Aston, Watson, and Whytlaw-Gray, Patterson and Cawood (see report for 1931) escaped notice by the Committee in preparing the report for 1931.

Lanthanum — Baxter and Behrens[14] have determined the atomic weight of lanthanum by analysis of lanthanum bromide. Lanthanum ammonium nitrate which had already been brought to a high state of purity in an earlier investigation was subjected to thirty series of fractional crystallizations. After conversion to bromide this salt was carefully dehydrated in a current of dry nitrogen and hydrogen bromide in such a way that melting of the hydrate was avoided, and the salt was finally fused in an atmosphere of pure hydrogen bromide. After being weighed the salt was dissolved and compared with silver in the conventional way and finally the silver bromide was collected and weighed. The following table gives weights corrected to vacuum. The fractions of lanthanum are numbered in the order of increasing solubility of the double nitrate, No. 371 representing the head fraction of the last series of crystallizations.

THE ATOMIC WEIGHT OF LANTHANUM

Fraction	Wt. of $LaBr_3$	Wt of Ag	Ratio $LaBr_3:3Ag$	At. wt. of La	Wt. of AgBr	Ratio $LaBr_3:3AgBr$	At wt. of La
376	4.01090	3.42801	1.170037	138.923	5.96743	0.672132	138.923
379	5.19186	4.43727	1.170057	138.929	7.72475	.672107	138.909
372	6.57727	5.62133	1.170056	138.929	9.78548	.672146	138.931
371	6.38414	5.45612	1.170088	138.939	9.49843	.672126	138.920
372	6.91830	5.91287	1.170061	138.931	10.29285	.672146	138.931
371	6.19359	5.29339	1.170041	138.924			
		Average	1.170057	138.929		.672131	138.923

The average value of the two methods, 138.926, is slightly higher than the value previously found by Baxter, Tani and Chapin, corrected for a new determination of the density of lanthanum chloride, 138.916. The

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(12) Hönigschmid, *Naturwiss.*, 20, 659 (1932).

(13) Allen and Moore, THIS JOURNAL, 53, 2512 (1931).

(14) Baxter and Behrens, *ibid.*, 54, 591 (1932).

average, 138.92, is probably nearer the truth than that recently given in the International table and the atomic weight of lanthanum is therefore changed in the table from 138.90 to 138.92,

Thallium.—Briscoe, Kikuchi and Peel[15] have redetermined the atomic weight of thallium by comparison of the chloride with silver. The processes of purification consisted in repeated crystallization of thallous sulfate and chloride, prepared from (A) English thallium of unknown origin and (B) German thallium obtained from Westphalian pyrites. The novel feature of the investigation lies in the method of titrating the chloride with silver. A few milligrams (2–3) excess of silver was added in every case to the thallous chloride solution and after standing and settling the supernatant solution (6–7 liters) was decanted, evaporated to small bulk and the silver content estimated by titration with *n*/1000 thiocyanate. Vacuum weights are given in the following table.

THE ATOMIC WEIGHT OF THALLIUM

	Wt. of TlCl	Wt. of Ag	TlCl/Ag	At. wt.. Tl
English	2.41969	1.08861	2.22273	204.33
	4.97940	2.24067	2.22234	204.29
	4.90541	2.20686	2.22280	204.34
	4.90351	2.20608	2.22272	204.33
	4.90391	2.20615	2.22283	204.34
	6.27962	2.82533	2.22261	204.32
				204.33
German	5.05837	2.27554	2.22293	204.35
	5.25891	2.36607	2.22264	204.32
	9.53621	4.28987	2.22296	204.35
	10.01985	4.50788	2.22274	204.33
	7.25159	3.26254	2.22268	204.33
				204.34
English A	10.04965	4.52210	2.22234	204.29
	11.55090	8.19723	2.22251	204.31
	10.60756	4.77211	2.22282	204.34
	9.91726	4.46146	2.22288	204.35
	9.53722	4.29023	2.22300	204.36
	11.88154	5.34523	2.22283	204.34
				204.33
English B	9.49327	4.27091	2.22277	204.34
	9.91925	4.46205	2.22302	204.36
	10.43230	4.69329	2.22281	204.34
	10.06308	4.52668	2.22305	204.36
	9.07037	4.08074	2.22272	204.33
				204.35
			Average of all	204.34

Exception may be taken to the analytical method, which was adopted because of alleged uncertainty in the conventional nephelometric method of comparison. The large bulk of supernatant liquid and washings must

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(15) Briscoe, Kikuchi and Peel, *Proc.* ROY. *Soc.*, (London) **A133**, 440 (1931).

have contained many milligrams of dissolved silver chloride, since the excess of silver used was very small. The ultimate fate of this silver chloride is difficult to guess but it is hard to believe that the titration of the excess of silver was not seriously affected by it especially in view of the well-known disturbance of the thiocyanate titration of silver in the presence of silver chloride. In fact it is hard to understand why the excess of silver in the individual experiments was so small as actually found. The effect of this difficulty would be, however, to raise rather than lower the atomic weight of thallium so that it is surprising that the atomic weight found is lower rather than higher than that recently found by Honigschmid, 204.39.

One experiment in which the nephelometric method was used showed erratic behavior, the final result for the atomic weight of thallium being 204.43.

The ratio of thallium to thallous nitrate also was determined. Buttons of fused electrolytic thallium were polished with chamois, fused in hydrogen and bottled in nitrogen for weighing. Solution in nitric acid followed by repeated evaporation with oxalic acid and fusion of the residue failed to give a product of constant weight, so that the authors consider the method (Crookes) unreliable. The results of two experiments are given in which the final weight of thallous nitrate is employed.

Tl	$TlNO_3$	At. wt., Tl
12.08412	15.74910	204.42
12.33736	16.07846	204.46

The results of both methods seem of doubtful value.

Johnson[16] claims that the equal opalescence method of titrating halogen compounds with silver is insensitive and gives erroneous results, and that the silver halide is probably contaminated with adsorption products. A new method of finding the end-point is proposed, by comparing the test solution with standard solutions of the reactants containing known amounts of silver and halide.

Wild[17] has compared the values for $1 + \lambda$ as found (1) by extrapolation of high pressure measurements of PV, (2) from low pressure measurements of PV, and (3) from gas density determinations. In computing the high pressure values the expression $PV = A + Bp + Cp^2 + Dp^4$ was employed. In case of the low pressure and density determinations the relation of PV to P is assumed to be linear.

HIGH PRESSURE

Observer	H_2	N_2	O_2	He	Ne	A
Onnes	0.99942	1.00041	1.00096	0.99949	0.99959	
Holborn and Otto	.99938	1.00046	1.00098	.99947	.99952	1.00098
Verschoyle	.99937	1.00049				
Average	.99939	1.00045	1.00097	.99948	.99956	1.00098

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(16) Johnson, *J. Phys. Chem.*, **35**, 540, 830, 2237, 2681 (1931); 86, 1942 (1932).

(17) Wild, *Phil. Mag.*. **12**, 41 (1931).

Observer	H_2	N_2	O_2	He	Ne	A
			LOW PRESSURE			
Chappuis	0.99942	1.00043				
Gray and Burt			1.00097			
Geneva Lab.	0.99935	1.00043	1.00086			
Heuse and Otto	,99942	1.00048	1.00097	0.99948	0.99953	1.00094
Average	.99940	1.00045	1.00093	.99948	.99953	3.00094
			DENSITY			
Baxter and Starkweather		1.00040	1.00093		0.99941	1.00107
Final mean	0,99939	1.00044	1.00094	0.99948	.99951	1.00099

Atomic Weights from Isotopes

A comprehensive report of the German Chemical Society by Hahn[18] covers the year 1931.

The question of the conversion factor from the physical to the chemical scale still seems to be unsettled. Birge and Menzel[19] prefer the Mecke and Childs value, 1.00022, to that of Babcock and Naudé, 1.00012. Aston[20] has been successful in photographing the lines of $O^{16}O^{17}$ and $O^{16}O^{18}$ of sufficient intensity for comparison with O_2^{16}. From the relative intensities 1 : 4 : 1072 the relative abundance of O_{17}, O_{18} and O_{16} is 0.24 : 1 : 536, a result which seems to support the ratio of O^{18} to O^{16} found by Mecke and Childs, 1 : 630. Since the accuracy of the mass spectrograph is admittedly no greater than $^1/_{10,000}$ and the uncertainty of the conversion factor obviously is as large, while the measurement of isotopic ratios has inherent uncertainties, the degree of precision of the determination of atomic weights from mass spectrographic data still seems to be inferior to that of the best chemical methods, although the striking concordance of the two methods in most cases is reassuring.

Recent results obtained by Aston[21] with the mass spectroscope are given in the following table. The factor used for conversion from the physical to the chemical basis is 1.000125.

Hydrogen.—Urey, Brickwedde and Murphy,[22] by spectroscopic examination of the least volatile fractions remaining from the evaporation of large quantities of liquid H_2, have detected the lines corresponding to the principal series of H^2. Examination of the spectrum of ordinary hydrogen indicated the proportion to be approximately 1 in 4000. Bainbridge[23] finds the mass of H^2 to be 2.01353 assuming He = 4.00216 and H^1 = 1.00778. The atomic weight of hydrogen is therefore slightly higher than the value for H^1 found by Aston.

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(18) Hahn, *Ber.*, **65A**, 1 (1932).

(19) Birge and Menzel, *Phys. Rev.*, **37**, 1669 (1931).

(20) Aston, *Nature*, 130, 21 (1932).

(21) Aston, *Proc. Roy. Soc.* (London), **A134, 571** (1932); *Nature*, 138, 221 (1931); **128**, 725 (1931); **129**, 649 (1932).

(22) Urey, Brickwedde and Murphy, *Phys. Rev.*, 89, 164 (1932).

(23) Bainbridge, *ibid.*, 41, 115 (1932).

	Isotopic weights and percentages							Packing fraction	At wt.
Lithium	6	7						20×10^{-4}	6.928
	91.7	8.3						17×10^{-4}	
Scandium	45							-7×10^{-4}	44.96
	100							assumed	
Rubidium	85	87						-8.2×10^{-4}	85.43
	75	25						assumed	
Strontium	86	87	88					-8.2×10^{-4}	87.64
	10	6.6	83.3					assumed	
Cesium	133							-5×10^{-4}	132.91
	100								
Barium	135	136	137	138				-6.1×10^{-4}	137.43
	5.9	8.9	11.1	74.2					
Thallium	203	205						1.8×10^{-4}	204.41
	70.6	29.4							
Lead (common)	203	204	205	206	207	208	209	$0\text{–}1 \times 10^{-4}$	207.19
	(0.04)	1.50	(0.03)	27.75	20.20	49.55	(0.85)		
Lead (Katanga)				206	207	208		$0\text{–}1 \times 10^{-4}$	206.067
				93.3	6.7	0.02			
Lead (Wilberforce)				206	207	208		$0\text{–}1 \times 10^{-4}$	206.20
				85.9	8.3	5.8			
Lead (Norwegian Thorite)				206	207	208		$0\text{–}1 \times 10^{-4}$	207.895
				4.6	1.3	94.1			
Uranium	238								
	100								

ATOMIC WEIGHTS

1933

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.93	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.10
Carbon	C	6	12.00	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	186.31
Chromium	Cr	24	32.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.3	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.3	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.4
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	83.7	Uranium	U	92	238.14
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.22	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

Lithium.—Van Wijk and van Koeveringe[24] and Nakamura[25] from a study of band spectra find a low value for the isotopic ratio of Li^7 to Li^6, and the corresponding atomic weight 6.89.

Boron.—Elliott[26] by a study of the band spectrum of boron monoxide finds the isotopic relationship 3.63 and the atomic weight 10.794.

Lithium, Sodium, Potassium, Cesium.—Bainbridge,[27] using a Dempster mass spectrograph, finds the ratio of the abundance of the lithium isotopes to be independent of the temperature of the source of the ions. The abundance ratio was determined in three experiments to be 10.75, 11.28 and 11.51, average 11.18, while Aston finds the ratio 11.

Sodium was found to contain less than $^{1}/_{3000}$ of Na^{21} or Na^{25} and less than $^{1}/_{800}$ of Na^{22}, if any, while potassium was found to be free from more than $^{1}/_{1500}$ of K^{43}, $^{1}/_{600}$ of K^{42} and $^{1}/_{300}$ of K^{40} referred to K^{39}.

Bainbridge[28] supports Aston's conclusion that the cesium mass spectrum is simple. The discrepancy between the atomic weights determined by chemical and physical methods is far larger than the apparent error of either.

Zinc.—The mass spectrum of zinc[29] obtained with a new form of discharge tube which avoids the presence of zinc hydrides gave no evidence of the isotopes Zn^{65} and Zn^{69} reported by Aston. The atomic weight recalculated from Aston's ratios, assuming the relation of the metallic line to the corresponding hydride to be that of the lines 64 and 65 in Aston's spectra, is found to be 65.33, with the conversion factor 1.00022.

Tellurium.—Additional isotopes of tellurium[30] of mass numbers 122, 123, 124 (and 127?) were discovered, the mass numbers and percentages of the complete spectrum being as follows

122	123	124	125	126	127	128	130
2.9	1.6	4.5	6	19.0	?	32.8	33.1

With Aston's packing fraction -5×10^{-4} and the conversion factor 1.00022 the atomic weight of tellurium is calculated to be 127.58, a value in much closer agreement with the chemical value than Aston's, 128.03.

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(24) Van Wijk and van Koeveringe, *Proc.* Roy. *Soc.* (London), **A132**, 98 (1931).

(25) Nakamura. *Nature*, **128**, 769 (1931).

(26) Elliott, *Z. Physik*, **67**, 76 (1931).

(27) Bainbridge, J. *Franklin Inst.*, **212**, 317 (1931).

(28) Bainbridge. Phys. *Rev.*, 36, 1668 (1930).

(29) Bainbridge, *ibid.*, 39, 847 (1932).

(30) Bainbridge, *ibid.*, 39, 1021 (1932).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OX PRINCETON UNIVERSITY]

Polarity in Certain Hydrocarbon Vapors

BY K. B. MCALPINE AND C. P. SMYTH

The measurements in the present paper were carried out in order to examine closely certain important molecules possessing little or no polarity. The dipole moments have been calculated from the dielectric constants determined for the substances in the vapor state, the familiar Debye equation being used. In this equation[1]

$$P = a + b/T \tag{1}$$

the polarization $P = \frac{\epsilon - 1}{\epsilon + 2} V$, where ϵ is the dielectric constant and V the molar volume. For an ideal gas, $V = RT/p'$, so that the polarization may be written

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{RT}{p'} \tag{2}$$

The actual pressure p of a gas under observation may be corrected to the pressure p', which it would exert if it were in the ideal condition and occupying the volume V, by means of the equation

$$p' = p\left[1 + \frac{p}{RT}\left(\frac{a}{RT} - b\right)\right] \tag{3}$$

This equation is derived simply from the van der Waals equation, a and b being the constants of this latter equation, different from the a and b of the Debye equation. Putting in numerical values

$$P = 62{,}371 \left(\frac{\epsilon - 1}{\epsilon + 2}\right) \frac{T}{p'} \tag{4}$$

where p' is expressed in millimeters.

Experimental Method

As the apparatus employed in measuring the dielectric constants was similar in many respects to that used by Zahn,[2] no detailed explanation of the symbolic diagram of it in Fig. 1 is given. Two circuits, I and II, were maintained in a condition of sustained oscillation by electron tubes, the wave length used being about 500 meters, corresponding to a frequency of 6 X 10^5. The individual frequencies were adjusted so that a beat note of 1000 cycles was produced, which could be picked up by a detector–amplifier system and compared with the 1000 cycle note emitted by a Leeds and Northrup hummer. The reference beat note, relative to which all adjustments in the measuring condenser system were made, was the frequency of the hummer, the identity of the beat note between the oscillators and the note emitted by the hummer being indicated by the absence of throbbing in the ear phones. The two oscillatory circuits were shielded by enclosure in large, wooden boxes covered with galvanized iron. Precise adjustment of the frequency of circuit II was made by turning a grounded brass disk D in such a way as to vary its distance from the circuit, changes of a small fraction of a cycle per second being thus securable. All adjustments of the condensers and switches were made from the outside by means of glass rods passing through the boxes.

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(1) *Cf.* Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).
(2) Zahn, *Phys. Rev.*, **24**, 400 (1924).

The gas condenser C in Fig. **1** consisted of two concentric cylinders, of pure copper tubing, 0.3 cm. thick and **13.4** cm. long, the outer grounded cylinder having an external diameter of 6.1 cm. and a separation from the inner of 0.07 cm. The cylinders were, at first, gold-plated, but, as the plate developed imperfections at the higher temperatures used, it was ground off and the pure copper surface employed. When not in use, the apparatus was kept filled with nitrogen to prevent gradual oxidation of the copper. The ends of the inner cylinders were fastened with silver solder and a copper rod holding it in place was insulated from the outer cylinder by quartz rings. The outer cylinder was wrapped with a thin sheet of mica, around which was wound a platinum resistance thermometer. The leads from the thermometer coil and those from the condenser were silver-soldered to tungsten wires, which were sealed through four tubes at the top of the thick-walled 65 mm Pyrex tube T enclosing the condenser (Fig. **2**). Two of these tubes and the **2** mm. capillary D leading to the vacuum system are shown in Fig. 2. The tube T was mounted in a cylindrical electrostatic shield S, closed at the bottom to prevent oil from coming up around the lead tubes. To prevent convection currents within the shield at high temperatures, it was found necessary to provide the top of the shield with a coil H, heated by direct current, which was completely shielded from the ungrounded lead U of the condenser by means of grounded brass plates P. S was bolted securely to a cover consisting of two sheets of *6*.4 mm. asbestos **A,** reinforced by a grounded sheet of **3.2** mm.

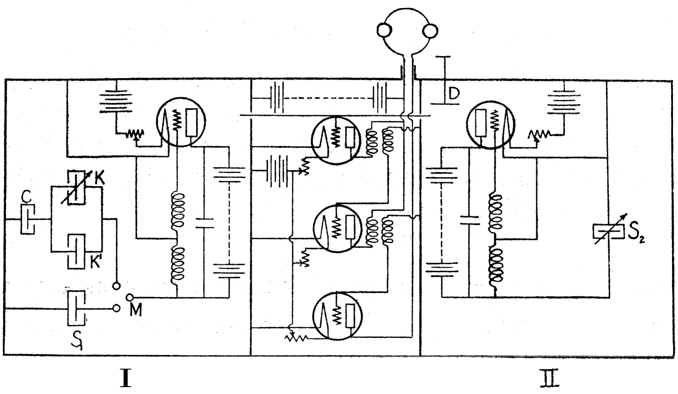

Fig. 1.—Diagram of circuits.

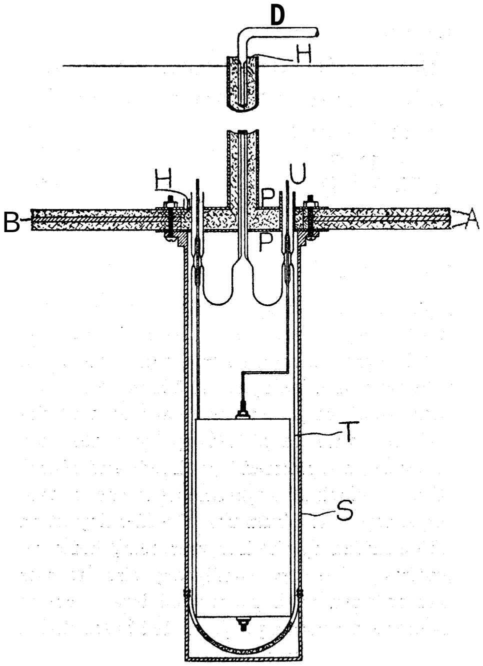

Fig. 2.—Gas condenser and shield.

brass B. The whole was then mounted in a large shielded box into which a large oil heating bath or toluene cooling bath could be inserted without introducing capacity effects. To prevent radiation from the oil-bath from reaching the rest of the oscillatory circuit, the condenser box was situated outside the main generator box, the lead from the condenser being brought through **an** opening in the latter box and supported by a notched sheet of mica fastened over the opening.

Because of small changes in the distributed capacity and inductance of the oscillatory circuits resulting from changes in the room temperature, the filament heating current, and the plate voltage, the beat oote between the oscillators showed a slow and often irregular drift in frequency. In order, therefore, to provide a reference capacity which could be considered as constant during the period of a run, a **1000** $\mu\mu$**f.** variable air condenser S_1 (Fig. **1)** was set in an electrostatic shield immersed in an oil-bath and so connected that the turn of a mercury switch M substituted it in circuit **I** in the place of the gas condenser system. The beat note could then be brought back to **1000** cycles by adjustment of D in circuit **II**.

For the manipulation of the gases, a system of reservoirs, traps, and purification tubes was used in connection with a mercury vapor pump. The gas pressure was read on a large mercury manometer provided with a steel scale. Liquids were vaporized in the apparatus from a U-tube which served as a pressure gage in the manner described hy Zahn.[3]

The gas cell C was connected in series with the two parallel capacities *K* and *K'*, *K* being a General Radio Company Type **222** variable precision condenser of **1500** $\mu\mu$f. capacity. The capacity *C* of the gas condenser when evacuated is made up of a geometrical capacity C_0, which becomes ϵC_0 when gas is admitted, and a fixed capacity L dependent upon the leads and insulators. When gas is admitted to *C*, the increase in its capacity *AC* must be balanced by a change *AK* in *K* in order to hold the frequency constant. The dielectric constant ϵ of the gas is then given by the expression

$$\epsilon - 1 = \frac{C^2}{C_0} \frac{(-\Delta K)}{(K + K' + C)\Delta K + (K + K')^2} \qquad (5)$$

in which the value of AK is **negative.**[2]

The precision condenser *K* was very carefully calibrated in position in the apparatus by a method similar to that previously described by one of the **writers.**[4] The condenser scale divisions, of which there were **2500,** were used as convenient units of capacity. The probable error in *AK* was **0.3** scale division. At first, *K'* consisted of three mica condensers of **1200, 2400** and **4800** $\mu\mu$**f.** capacity in parallel, but as these condensers showed a slight, irregular variation in capacity with the passage of time they were replaced by two variable air condensers, which showed no change with time. The capacity of these two condensers, which were used at their maximum value, was determined by a careful step-by-step calibration as K' = **7097 ± 2** scale divisions on the precision condenser.

The fixed capacity through the quartz insulators in the gas condenser was calculated from the dimensions and the known dielectric constant of quartz as **7.3 ± 0.7** scale divisions. The capacities of the various leads were very carefully determined by the usual methods of short-circuiting or disconnecting the condensers and of setting up imitation leads. The values expressed in scale divisions for the different capacities involved were *C* = **448.6 + 0.7, L = 23 3 + 1.4,** C_0 = **425.3 * 2.1.** An attempt made to determine C_0 and L in the manner commonly used in measurements on liquids by measuring the cell empty and again filled with pure benzene gave less accurate results and was abandoned. The value of *K* needed in the equation for $\epsilon - 1$ was determined

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(3) Zahn, *Rev. Sci. Instr.*, 1, 299 (1930).

(4) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc , New York, 1931, p. 52.

for a number of settings on the high part of the scale by tuning the oscillators to zero beats, short-circuiting C, and changing K by an amount ΔK until the original frequency was restored. K was then calculated from the equation for series capacities. When all the errors in the calibration and capacity determination are taken into account, it appears that the probable error in the absolute value of $\epsilon - 1$ arising from these causes is 0.9%. The relative error from these causes should be less than 0.2%.

During the course of a run the temperature of the gas cell was maintained constant to 0.02° by means of the bath surrounding it. This control was necessitated by the excellent thermal insulation which, unfortunately, existed between the two cylinders of the condenser. A rapid temperature rise of as much as 0.2° caused an unequal expansion of the two cylinders with a resulting change in capacity, and the temperature change resulting from change in gas pressure made it necessary to delay a capacity reading for half an hour after the pressure change had been effected in order that the temperature might become uniform.

The difficulty of temperature equalization made it impossible to obtain an accurate value for the capacity of the evacuated condenser directly. In the most satisfactory method of obtaining it a reading was taken on the precision condenser with the gas or vapor in the condenser at 20–30 mm. pressure and another at 100–150 mm. When these two precision condenser readings were plotted against p' and a straight line drawn through the points, the intercept of the line at $p' = 0$ gave the vacuum reading. The values of $(\epsilon - 1)/(\epsilon + 2)$ were then calculated directly. When working with vapors at low temperatures, measurements were made at several pressures in order to detect possible condensation. The values of $(\epsilon - 1)/(\epsilon + 2)$ were then plotted against the corrected pressures p'. Any condensation was evidenced by a departure of the points for high pressure from the straight line through the lower points. The effect of any drift in the circuits outside the gas condenser was eliminated by repeating every run in the reverse direction.

In order to determine by actual experiment the accuracy of the measurements, a large number of determinations were made upon air carefully dried and purified by passage through a soda lime tower, and upon carbon dioxide, taken from a cylinder and repeatedly fractionated by condensation with liquid air. The values of $\epsilon - 1$ were reduced to 0° and 760 mm., the perfect gas law being employed for air and the van der Waals equation for carbon dioxide. For air, the average deviation from the mean of twenty-three measurements was 0.41%, and, for carbon dioxide, the average deviation in twenty-one measurements was 0.33%. The values have been compared with the results of fifteen other investigations, of which the two most extended and reliable gave the values shown in Table I for comparison with those of the present investigation. At the bottom of the table are the values of $n_\infty^2 - 1$, n_∞ being the index of refraction extrapolated to infinite wave length. Since, for carbon dioxide, correction has been made for infra-red absorption[6] and since, for air, this absorption can be neg-

TABLE I

VALUES FOR AIR AND CARBON DIOXIDE

	$(\epsilon - 1) \times 10^6$		
	CO_2	Air	CO_2/Air
Zahn[2,6]	972	572	1.700
Stuart[7]	987	582	1.696
McAlpine and Smyth	989	581	1.702
$(n_\infty^2 - 1) \times 10^6$	975[5]	575[8]	1.696

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(5) Fuchs, Z, *Physik*, 46, 519 (1928)

(6) Zahn, *Phys. Rev.*, Z7, 455 (1926).

(7) Stuart, Z. *Physik*, 47, 457 (1928).

(8) "International Critical Tables," Vol. VII, p. 5.

lected, $n^2_\infty - 1$ should, in the absence of a dipole moment, be identical with $\epsilon - 1$. The ratio of the value for carbon dioxide to that for air is given in the last column.

The results of the present investigation are approximately 1.5% higher than those of Zahn but differ by less than the small average deviation from the mean from the more recent results of Stuart. The close agreement of the ratio with Zahn's ratio shows the difference in the absolute values to be a matter of the respective calibrations, as this difference is within the limits permitted by the errors assigned to the two calibrations. The recent determination of $(\epsilon - 1) \times 10^6$ for nitrogen, 589, by Andrews[9] is higher than Zahn's value 580 by just the same amount as the difference between the value for air in the present work and that of Zahn. It appears probable, therefore, that the values of $(\epsilon - 1) \times 10^6$ for air and carbon dioxide are slightly higher than those given for $(n^2_\infty - 1) \times 10^6$.

Purification of Materials

Benzene.—Merck's C. P. crystallizable benzene was shaken repeatedly with concentrated sulfuric acid, water, dilute sodium hydroxide, and more water, dried over calcium chloride, and crystallized three times (m. p. 5.50°). It was then refluxed over phosphorus pentoxide, distilled, refluxed over sodium wire, and distilled again; b. p. 80.2°; n^{25}_D 1.49823.

Toluene.—Merck's C. P. toluene was washed with concentrated sulfuric acid, water, dilute sodium hydroxide solution, and again with water, shaken with pure mercury, filtered, and dried first with calcium chloride, then with phosphorus pentoxide, and, finally, by refluxing over molten sodium and subsequent distillation; b. p. 110.5°; n^{20}_D 1.4955. A second portion treated in the same way, except for the omission of the refluxing over sodium, had the same constants. A third portion was treated like the first except that between the drying with calcium chloride and that with phosphorus pentoxide, it was crystallized in an ether-bath maintained at –105–110°; b. p. 110.5–6°; n^{20}_D 1.49564. This was distilled directly from the sodium into the gas system of the apparatus for the dielectric constant measurements.

Propane and **Propylene.**—Gases of high purity from the Linde Air Products Company were passed through phosphorus pentoxide into the gas system of the apparatus, where they were repeatedly fractionally distilled.

Experimental Results

When $(\epsilon - 1)/(\epsilon + 2)$ is plotted against p', which is obtained by use of equation (3), the values of the van der Waals constants being taken from Landolt–Bornstein, the slope of the resulting straight line is used to calculate the polarization, since, from equation (4), it follows that

$$P = 62{,}371\ T\Delta\frac{\epsilon - 1}{\epsilon + 2}/\Delta p' \qquad (6)$$

A line was obtained at a given temperature by determining points from pressures of 10–30 mm. up to 800–1100 mm., then down to low pressure again to make sure that no change had occurred during the course of the run. Several such runs were made at each temperature and a value of P obtained from the line for each run, The average value at each tempera-

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(9) Andrews, *Physics*, 1, 366 (1931).

TABLE II

MEAN VALUES OF P AND PT

T, °K.	P	PT	T, °K.	P	PT
	Benzene			Toluene	
325.9	26.87	8,757	357.3	34.86	12,455
375.1	27.13	10,176	378.9	34.62	13,118
428.8	27.04	11,594	431.8	34.46	14,880
480.1	26.99	12,940	481.7	34.20	16,474
	Propane			Propylene	
226.7	16.00	3628	245.5	18.76	4606
246.5	16.19	3992	246.1	18.79	4623
293.3	16.11	4726	272.2	18.45	5021
352.4	16.02	5647	303.8	18.18	5523
413.3	16.04	6627	352.2	17.77	6258
485.9	16.07	7810	406.8	17.59	7154
			476.2	17.29	8233

ture given in Table II was used to calculate the values of PT, which, in Fig. 3, are plotted against T. The method of least squares was used to

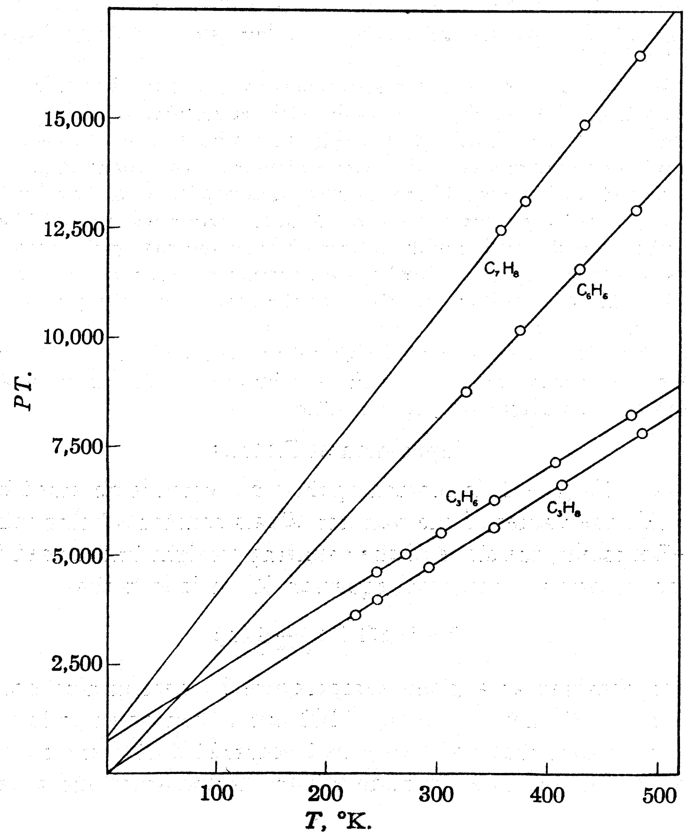

Fig. 3.—PT–T curves.

calculate the values of the constants in equation (1), which are given in Table III. The value of the refraction for infinite wave length, P_E, was obtained by extrapolation from the dispersion data for liquids in Landolt-Börnstein and the values given for the atomic polarization calculated as $P_A = a - P_E$. The electric moment μ was calculated from b as $\mu = 0.0127 \times 10^{-18} \sqrt{b}$, the probable error in the two virtually zero values being 0.05×10^{-18}, and in the other values 0.02×10^{-18}.

TABLE III

VALUES OF FUNDAMENTAL CONSTANTS

Substance	a	P_E	P_A	b	$\mu \times 10^{18}$
C_6H_6	27.0	25.1	1.9	−18	0
C_7H_8	32.5	29.8	2.7	841	0.37
C_3H_8	16.0	15.7	0.3	18	0
C_3H_6	15.7	15.1	.6	745	0.35

After the submission of these results for publication, a new method for the elimination of error due to deviation from the ideal gas laws was adopted in later work to be described elsewhere. Polarizations calculated by means of the ideal gas law are plotted against the pressure and the curve thus obtained is extrapolated to zero pressure to obtain a polarization value unaffected by deviations from the ideal gas law. In propane and propylene, the deviations are so small that the different method of calculation leaves the results in Table II unaltered. For benzene, the polarization values are lowered about 0.5% by the new method of calculation and, for toluene, about 1.2%. The changes in the constants calculated from these polarizations are shown below to be negligible or almost so.

BENZENE			TOLUENE		
T, °K.	P		T, °K.	P	
325.9	26.77	$a = 27.0$	357.3	34.46	$a = 32.3$
375.1	26.94	$b = -55$	378.9	34.18	$b = 740$
428.8	26.96	$\mu = 0$	431.8	34.02	$\mu = 0.35 \times 10^{-18}$
480.1	26.84	$P_A = 1.9$	481.7	33.84	$P_A = 2.5$

Discussion of Results

The mean value, 27.01, of the polarization of benzene vapor, which is independent of temperature, is slightly higher than the values for the liquid, 26.62 at 10° and 26.78 at 60°,[10] which increase slightly with rising temperature, and lower than the value for the solid, 28.5 at 0°, found by Morgan and Lowry. The absence of variation with temperature in the polarizations of benzene and of propane is in contrast to the small but definite increase observed in liquid benzene and in marked contrast to the uniform increase observed in all the liquid paraffins which have been studied over a wide range of temperature.[11] This difference in behavior between the liquid and the vapor is important since it shows that the increase in polarization with rising temperature in the liquid cannot be due to any direct intramolecular effect of temperature, for such an effect would be

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[10] Morgan and Lowry, *J. Phys. Chem.*, **34**, 2386 (1930); Smyth and Stoops, THIS JOURNAL, 61, 3312 (1929); Smyth and Walls, *ibid.*, 64, 1854 (1932).

[11] (a) Smyth and Stoops, *ibid.*, 60, 1883 (1928); (b) Smyth and Dornte, *ibid.*, **52**, 3546 (1930).

apparent in the gas also. As the values of P_E for benzene and toluene are calculated directly from measurements on the liquids and those for propane and propylene as the sum of the atomic refractions obtained from measurements on liquids, it is evident that the values of P_A must be regarded as approximate. The most accurate measurements on the refraction of benzene vapor,[12] when extrapolated to infinite wave length, give a value 26.22 for P_E, which gives $P_A = 0.8$, possibly more accurate than the value in Table III and lower than the values 1.5–1.9 obtained as the difference between the solid and the liquid. Similar use of the refractive index determined for propylene by Trautz and Winkler[13] gives $P_A = 1.0$, higher than the value in Table III. The discrepancies among the results of different investigators of the refraction of vapors make it doubtful whether the P_A values obtained by using the values of the vapor refractions are more accurate than those in Table III, which are certainly comparable with one another.

Krchma and Williams[14] and Williams and Ogg[15] measured benzene in three different solvents, obtaining for the polarization in carbon tetrachloride, 26.7, in carbon disulfide, 28.5, and in hexane, 27.8, and, from these values, using $P_E = 25.8$ and neglecting P_A, values of 0.06×10^{-18}, 0.09×10^{-18}, and 0.08×10^{-18} for the moment of the benzene molecule. An error occurred in these calculations for recalculation from the same data gives 0.21×10^{-18}, 0.39×10^{-18}, and 0.31×10^{-18}, values slightly higher than the figure 0.2×10^{-18}, calculated previously by one of the writers as a value indistinguishable from zero by the method employed.[16] Although it has been generally assumed that the moment of the benzene molecule is zero,[17] it is reassuring to obtain definite experimental evidence that it is within 0.05×10^{-18} of zero. The negative value, -18, of b in Table III has no significance nor has the positive value 18 for propane, both showing merely that the value of the moment is within 0.05×10^{-18} of zero.

The propane molecule may be pictured as a tetrahedral carbon atom with hydrogens on two apices and methyl groups on two. Two planes of symmetry perpendicular to one another may be drawn through the central carbon atom, but, when a third plane perpendicular to these two is drawn, it is apparent that the two hydrogens are on one side of it and the two methyl groups on the other. Because of the tetrahedral angle, any moment in a C–H bond of one of the methyl groups has a component in the direction of the C–C line equal to one-third of its value. The three C–H bonds of the group have, therefore, a resultant moment equal to that of a single C–H bond. The moments in the C–H bonds of the methyl groups

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(12) Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math*, **2**, No. 13, 1 (1925).

(13) Trautz and Winkler, *J. prakt. Chem*, *104*, 44 (1922).

(14) Krchma and Williams, This Journal, 49, 2408 (1927).

(15) Williams and Ogg, *ibid.*, 50, 94 (1928).

(16) Smyth, *ibid.*, 46, 2151 (1924).

(17) See Ref. 4, p. 106.

would, consequently, cancel moments of equal size in the two C–H bonds on the central carbon and any moment in the molecule as a whole would have to arise from polarity in the C–C bonds, from inequality in the moments of the C–H bonds of the primary and secondary carbons, or from distortion of the tetrahedral structure by repulsion in such a way as to prevent compensation of the moments of the two central C–H bonds by those of the methyl C–H bonds. If propane had the maximum moment, 0.05×10^{-18}, permitted to it by the accuracy of the measurements, it would be equivalent to the effect of the displacement of a pair of electrons 0.005 Å. from a position of symmetry. Although it is likely that the propane molecule may have a very small moment, it is evidently so small that any polarity in the C–C bonds, electrical dissymmetry caused by repulsion between the different parts of the molecule or difference in electronegativity between the hydrogens on the secondary and those on the primary carbons may be regarded as undetectable by means of the electric moment. This result is in harmony with the absence of any detectable moment in the isomers of heptane and with the consequent absence of variation in the electronegativities of the alkyl radicals detectable by this means.[11a]

The value obtained for the moment of toluene is in excellent agreement with the very approximate value 0.4×10^{-18} found for the liquid.[14,16,18]

The closeness of the accurately determined value[19] for a-butylene, 0.37×10^{-18}, to that for toluene in the present paper and to the 0.35×10^{-18} found for propylene are very striking. It is evident that, although the replacement of a hydrogen by a methyl group in a saturated aliphatic hydrocarbon gives rise to no moment, a similar replacement of a hydrogen attached to an unsaturated carbon gives rise to a definite electrical dissymmetry. Calculation shows that if the C–H bond has a moment of about 0.4×10^{-18} associated with it as commonly supposed,[20] inductive effects should give rise to moments of the magnitude found for these unsymmetrical molecules.

The writers wish to express their gratitude to Dr. C. T. Zahn for his advice on the construction of the apparatus.

Summary

An apparatus for the accurate measurement of the dielectric constants of gases and vapors has been constructed and tested by repeated measurements upon air and carbon dioxide. Values have been determined for benzene, toluene, propane and propylene and used to calculate their polarizations and electric moments.

The absence of any change in the polarizations of benzene and propane with rising temperature indicates that the increase previously observed

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(18) Williams, *Physik. Z.*, 29, 174 (1928); Williams and Krchma, THIS JOURNAL, 49, 1676 (1927)

(19) Smyth and Zahn, *ibid.*, 47, 2501 (1925).

(20) Ref. 4, p. 117.

with rising temperature in a number of liquid paraffins is due to decrease in intermolecular action.

The zero moment found for the benzene molecule agrees with the less accurate results of the measurements upon the liquid and with the symmetrical structure of the molecule. The zero moment found for propane is consistent with the absence of moment in the higher members of the series and shows that any polarity in the C–C bonds, electrical dissymmetry caused by repulsion in the molecule or difference in electronegativity between the hydrogens on the secondary and those on the primary carbons is too small for detection by means of the electric moment.

The small moments found for toluene and propylene are of the same magnitude as those which might arise from inductive effects in the molecules.

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The Possibility of Dipole Rotation in Certain Crystalline Solids

BY S. E. KAMERLING AND C. P. SMYTH

This paper presents the results of an investigation undertaken with the object of studying a possible contribution to the dielectric constants of certain substances through the rotation of a polar group in a molecule fixed in a crystal lattice or through the rotation of the entire molecule in the lattice, the latter possibility having been suggested by the results of Errera.[1,2] When the molecules of a substance are so fixed in the solid state that any dipoles contained by them are unable to orient at all in an externally applied electric field, the dielectric polarization of the substance consists only of the so-called optical part, $P_E + P_A$, which should be virtually independent of temperature and of frequency within the range ordinarily used in dielectric constant measurements. Any considerable variation of polarization with temperature or frequency should, therefore, be evidence of dipole orientation, that is, of rotation of polar groups or molecules in the solid. In the present measurements, a certain number of molecules are placed between the plates of a condenser by filling the condenser with liquid, which is then frozen. Consequently, as the temperature is lowered, the number of molecules between the plates is not appreciably altered by the changing density of the solid and the apparent value observed for the dielectric constant should not alter with the density. Although this apparent value of the dielectric constant evidently differs by a small but increasing amount from the true value as the temperature falls below the freezing point, it makes an excellent substitute for the polarization, which

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(1) Errera, *J. phys. radium*, [6] 5, 304 (1924).

(2) Smyth, "Dielectric Constant and Molecular Structure." The Chemical Catalog Company. Inc., New York, 1931, p. 38.

is hard to obtain because of the difficulty of measuring the densities of the low melting solids as well as the true dielectric constants.

Apparatus

The apparatus used in measuring the dielectric constants was the capacity bridge employed in a previously described investigation,[3] which was actually carried out after the measurements of the present paper Current of a pure sine wave form and of frequencies from 200 to 50,000 cycles was supplied to the bridge from an 8A Western Electric oscillator. At the higher frequencies, a six-tube amplifier with a detector and a multimeter as null instrument was used with the bridge, while, at lower frequencies, a two stage transformer-coupled audio frequency amplifier was employed. A resistance in series with the condenser in each of the two capacity arms of the bridge served to balance any conductance in the other capacity arm. As the only appreciable conductance occurred in the measuring condenser, the series resistance in the opposite arm provided a means of calculating the phase angle of this condenser.4 In the present work, however, only qualitative use has been made of this resistance. When it was large, *a* considerable error was introduced into the results by the capacities of the coils of the non-inductively wound decade box used as the series resistance.

The other apparatus and methods were similar to those described in previous papers from this Laboratory except in the modification of the measuring condenser and its use. A platinum resistance thermometer cased in glass was inserted inside the innermost of the three concentric gold-plated cylinders of the condenser. Before solidification of the liquid in the condenser, dissolved gas was commonly pumped off as far as possible with a water pump. In spite of this, the occurrence of gas pockets and cracks in the solid tended to lower the value observed for the dielectric constant. The solid was melted and slowly frozen again from the bottom up after the cell had been tapped to drive off gas bubbles. This process was repeated several times until an approximately constant value was reached for the dielectric constant, which was then measured at different temperatures below the melting point and at different frequencies. A 10 or 12% increase in the observed value might be brought about by these successive freezings The dielectric constant observed was evidently a minimum value, but the values observed for a given solid were fairly accurate relative to one another, except at the lowest frequencies where it was difficult to balance the bridge.

Preparation of Materials

n-**Heptyl** bromide was obtained as in earlier work.[5]

Anisole.—Kahlbaum anisole was dried with calcium chloride and fractionally distilled. The middle fraction boiling at 153.9–154.1° (769 mm.) was used; n_D^{20} 1.51732; d_4^{20} 0.9951.

Phenol.—Merck "Reagent" phenol was melted and fractionated The fraction boiling at 181.6° (756 mm.) was used.

Benzoyl Chloride.—Eastman Kodak Company benzoyl chloride was fractionally distilled. The middle portion was again distilled, the fraction boiling constantly at 197.9° being used; n_D^{20} 1.55354; m. p. −0 6°.

Experimental Results

The apparent values determined for the dielectric constants ϵ at the temperatures t and at various frequencies from 50 to 0.2 kilocycles are given

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(3) Smyth and Kamerling, THIS JOURNAL, 53, 2988 (1931).

(4) See Hague, "Alternating Current Bridge Methods," Sir Isaac Pitman and Sons, Ltd., London. 1923, p. 196.

(5) Smyth and Rogers, THIS JOURNAL, 52, 2227 (1930).

in Table I. In Table II the rounded values of ϵ at 50 k. c. and the densities obtained from various sources are used to calculate approximate values of the molar polarization, $P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$. The values of the atomic polarization P_A are obtained by subtracting from P the values of the electronic polarization P_E obtained by the extrapolation to infinite wave length of data on refraction taken directly from or calculated from material in Landolt–Bornstein (5th edition).[6]

TABLE I

DIELECTRIC CONSTANTS OF SOLIDS

n-Heptyl Bromide (m. p. − 60°)

t, °C.	50	30	10	5	1	0.2 k. c.
−64.0	2.82	2.82	2.83			
−62.3	..	..	..	No change		

Hydroquinone Dimethyl Ether (m. p. 55.2°)

t, °C.	50	30	10	5	1	0.2 k. c.
−91.0		2.80			2.81	
−30.8	2.81	2.81	2.81		2.81	
−14.8	2.81	2.81	2.82		2.82	2.82
1.6		2.82	2.82		2.82	2.82
29.2	2.82	2.82	2.82	2.82	2.83	2.83
36.3	2.82	2.82	2.82	2.82	2.83	2.83

Anisole (m. p. −37.8°)

t, °C.	50	30	20	10	5	1
−56.3	2.88	2.88		2.88		2.92

No change on cooling 10°

Phenol (m. p. 42.5°)

t, °C.	50	30	10	5	1	0.2 k. c.
−22.3	2.77	2.77		2.77	2.78	2.80
− 4.9	2.79	2.80	2.80	2.80	2.83	2.85
− 5.7	2.81	2.82	2.82	2.83	2.86	2.92
22.9	2.84	2.85	2.86	2.88	2.94	2.98
34	2.89	2.90	2.96	2.96	3.00	3.05

Benzoyl Chloride (m. p. −0.6°)

t, °C.	50	30	10	5	1	0.2 k. c.
−51.1	2.96	2.97	2.98	2.99	3.03	3.14
−31.7	3.02	3.04		3.10	3.14	
−20.3	3.09	3.12	3.12	3.22	3.29	
−10.4	3.33	3.44	3.55	3.64	4.0	

TABLE II

POLARIZATION OF THE SOLIDS

	ϵ	*d*	*P*	P_E	P_A
n-$C_7H_{15}Br$	2.8	1.23[a]	55	41.2	14
p-$C_6H_4(OCH_3)_2$	2.8	1.13[b]	46	40.8	5
C_6H_5OH	2.8	1.07[c]	33	27.5	5.5

[a] Extrapolated from the densities of the liquid: probably correct to better than 10%. [b] The average of five determinations with a pycnometer. [c] "International Critical Tables." Vol. I, p. 199.

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(6) *Cf.* Ref. 2, p. 23.

Discussion of Results

A rough attempt has been made to calculate P_A for heptyl bromide because of the surprisingly high value, 15.5, found for it by Smyth and Rogers by means of the variation of the polarization with temperature in solution.[5] The value in Table II is in excellent agreement with that given by the solution measurements, but, if the density of the solid were 10% higher, as is not impossible, the value of P_A given by the solid would drop to 8. The values of P_A for the other substances are of the magnitude usually found for polar molecules of fair size.[7]

The values in Table I show positively that heptyl bromide, hydroquinone dimethyl ether, and anisole give no dipole orientation in the alternating electric field in the ranges of temperature and frequency used. This means not only that the large polar molecules do not turn as a whole in the field but also that the polar CH_3—O group, which might be mobile about its bond to the ring, is not turned by the field. The results on phenol and benzoyl chloride are inconclusive. The dielectric constants increase somewhat with rising temperature and decreasing frequency of the field in the manner that might be expected if an occasional molecule or polar group attached to the ring were able to turn in the field. However, the same effects could arise from the displacement in the field of small amounts of ions, which would be more important as the melting point was approached and the frequency lowered. As phenol and benzoyl chloride are difficult substances to obtain in a very pure state, it appears probable that the small variation of dielectric constant observed is due to the presence of impurities rather than to any motion of the large molecules as a whole or of their polar groups.

Summary

A low frequency capacity bridge is used to measure the dielectric constants of certain crystalline solids over a range of temperature from the melting point down and at frequencies from 200 to 50,000 cycles. Heptyl bromide, hydroquinone dimethyl ether and anisole show no turning of the molecules or of their polar groups in the externally applied field, while, in phenol and benzoyl chloride, effects which might indicate such turning are attributed to the presence of small quantities of impurities. The atomic polarizations of three of these substances are calculated.

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(7) Ref. 2, p. 164.

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Application of the Gibbs Adsorption Theorem to Solid–Liquid Interfaces

BY F. E. BARTELL, F. L. MILLER AND E. G. ALMY

The Gibbs adsorption theorem expressed in the well-known approximate form[1]

$$u = -\frac{c}{RT} \times \frac{\mathrm{d}\,S_x}{\mathrm{d}\,c}$$

has been used by many different investigators in the study of adsorption at liquid–air and liquid–liquid interfaces. Although it has been assumed that the formulation should apply to liquid-solid interfacial systems, it has heretofore not been used because no method has been available for the measurement of the interfacial tension between a solid adsorbent and solution. The recent work of Bartell and Osterhof on adhesion tension[2] has made possible the application of a modified form of the equation to solid–liquid interfaces.[3]

Numerically, adhesion tension is the difference between two quantities which are themselves quite large but not directly measurable, namely, the surface tension of a solid, S_1, and its interfacial tension against a given liquid, S_{12}; *i. e.*

$$A_{12} = S_1 - S_{12}$$

The Gibbs theorem as applied to a solid–liquid interface would be expressed as follows

$$u = -\frac{c}{RT}\frac{\mathrm{d}\,S_{12}}{\mathrm{d}\,c}$$

The measurements made by the Bartell-Osterhof method give the values for A_{12}, but not those for S_{12}. However

$$S_{12} = S_1 - A_{12}$$

Therefore

$$u = -\frac{c}{RT}\frac{\mathrm{d}(S_1 - A_{12})}{\mathrm{d}\,c}$$

and since the surface tension of the solid is independent of the concentration of the solution, we have

$$\frac{\mathrm{d}\,S_1}{\mathrm{d}\,c} = 0, \text{ and}$$

$$u = +\frac{c}{RT}\frac{\mathrm{d}\,A_{12}}{\mathrm{d}\,c}$$

Accordingly, if the addition of solute tends to increase the adhesion tension of the solid–liquid system, it is to be expected that the solute will be pref-

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(1) In this equation u represents the excess concentration of the solute per sq. cm. of interface. and S_x refers to the interfacial tension at either a liquid–gas, liquid–liquid or liquid-solid interface. In this paper the different phases involved will be designated by the subscripts 1, 2 and 3, indicating solid and the different liquid phases, respectively. Thus S_0 = Surface tension liquid–gas (or air); S_{23} = Surface tension liquid–liquid; S_{12} = Surface tension solid–liquid.

(2) Rartell and Osterhof, Z. *physik. Chem.*, **130**, 715 (1927); *Ind. Eng. Chem.*, **19**, 1277 (1927).

(3) Bartell and Sloan, THIS JOURNAL, **51**, 1654 (1929).

erentially adsorbed at the interface, *i. e.*, positive adsorption demands that the term dA_{12}/dc be positive.

By measuring the adhesion tensions of a series of binary solutions against silica and applying the equation developed above, the adsorption at any concentration may be calculated. Such measurements and calculations have been carried out. In the systems studied the adsorbent in each case was silica and the liquid adsorbed was ethyl carbonate. Adsorption from each of three solvents, namely, benzene, α-bromonaphthalene and dimethylaniline, was investigated. All of the liquids were first purified, then twice distilled and that fraction coming over at constant temperature was used.

It has been frequently pointed out that the behavior of organic liquids at a silica surface is very similar to that at a water surface. The data presented herein will serve to test this statement. By applying Gibbs' equation to values of the interfacial tension between the binary organic mixtures and water, it is possible to calculate the adsorption at the water interface and to compare the values obtained with those for adsorption from the same systems at the silica interface. Such calculations and comparisons have been made and are included in the tables.

Experimental

Adhesion Tension.—The adhesion tension values for the different: solutions were determined by the Bartell–Osterhof[2] method, which consists in measuring the pressure of displacement of the solution by water from the minute pores formed in a tightly packed membrane of finely divided solid. From the equilibrium displacement pressure measured in the above manner, it is possible to calculate the adhesion tension of the solution against the solid by means of the equation

$$A_{12} = A_{13} - S_{23} \cos \theta_{23}$$

A_{13}, the adhesion tension for water against a given solid is specific for that solid; values had previously been determined for water against silica. These values for water were again checked. Cos θ_{23} was determined by the displacement pressure method mentioned above. With these data A_{12}, the adhesion tension of the second liquid system against the solid, was determined.

The solid used in this investigation was silica. It was Tripoli airfloat silica which had been treated several times with boiling 1–1 hydrochloric acid and repeatedly washed with boiling water after each treatment until no trace of acid was found in the filtrate. This treatment removed the impurities of iron and aluminum salts which were present in the original material. The final product contained less than 0.4% of impurities. All of the silica which would pass through a 350 mesh sieve was saved for this work. Before use the silica was heated in an electric muffle at about 950° for not less than two hours.

Interfacial Tension Determinations.—Measurements of the interfacial tensions of each of the solutions of the different binary systems were made by means of the double cylinder type of interfacial tension apparatus developed in this Laboratory.[4] These measurements were carried out in a small water thermostat, the temperature of which was maintained at 25 ± 0.05°.

The solutions of the different binary systems were made up accurately by weight. Concentrations are expressed in terms of mole fractions. The results obtained are given in Tables I, II and III (column 3).

The interfacial tension–concentration curves (plotted from the data) for each of the three systems were found to be smooth and regular. There was no evidence of a minimum point in any of the curves. The curves were concave upward, indicating preferential adsorption of ethyl carbonate at the water interface from each of the liquids which were used as solvents.

The adhesion tension–concentration curves were found to be similar to those expressing the interfacial tension data except that they were concave downward instead of upward. In the former case the slope d S_{23}/d c was negative, whereas d A_{12}/d c is positive. This is in agreement with the theoretical considerations discussed above. Just as in the interfacial tension–concentration curves there was no indication of any irregularity nor of a maximum point in any of the curves.

Calculation of Adsorption at Silica Interface.—If one plots the values of the adhesion tensions of ethyl carbonate solution–silica against the

TABLE I

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from Benzene[a]

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g. /sq. cm	A_{12} silica	Adsorption Et_2CO_3 u mole /sq. cm. At silica interface	Adsorption Et_2CO_3 u mole /sq. cm. At water interface	Area of molecules sq. cm. X 10^{16} At silica interface	Area of molecules sq. cm. X 10^{16} At water interface
0.000	0.8741	34.65	404.1	51.08	...		...	..
.038	.8784	31.32	350.6	55.29	1 287	0 472	15 42	22.1
.027	.8843	29 30	318.0	57.86	1.824	1.663	16.76	14.8
.113	.8880	27.60	294.9	59.73	2.207	2 115	17 42	13.3
.182	.8952	24.99	259.6	62.45	2.655	2.462	18.17[b]	16.9[b]
.301	.9080	21.99	216.1	6587	3.025	2.817	19.09	180
.424	.9203	19.74	190.9	68.21	3.305	3.398	19.16	17.4
.506	.9278	18.42	172.6	69.29	3.491	3.826	19 06	17.0
.686	.9444	16.01	144.0	71.53	3.672	4.165	19 07	17.1
.864	.9590	13.92	124.3	73.08	3.814	4.600	1900	171
.929	.9641	13.16	115.5	73.77	3.814	4 600	19.09	17.5
.985	.9683	12.71	110.5	74.16	3.814	4 600	19.16	17.5
1.000	.9691	12.61	109.4	74.25	3.814	4.600	19.09	17.5
						Average	19.0	17.3

[a] Radius of silica membrane pore = 1.602 X 10^{-4} cm. A_{13}, water against silica = 82.86 dynes/cm. [b] Values below b in each case were used in obtaining averages.

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(4) Bartell and Miller, THIS JOURNAL, 50, 1961(1928).

TABLE II

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from a-Bromonaphthalene

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g./sq. cm	A_{12} silica	Adsorption Et_2CO_3 u mole/sq. cm At silica interface	 At water interface	Area of molecules sq. cm. × 10^{16} At silica interface	 At water Interface
0.000	1.497	41.84	512.3	42.60	...	...	..	..
.014	1.491	38.55	467.5	46.11	0.549	0.872	23.3	16.7
.052	1.473	34.51	407.7	50.81	2.502	1.800	14.2	17.2
.101	1.449	30.85	352 0	55.19	3.107	2.510	16.2	17.8
.236	1.383	24.84	259 6	62.45	3.107	3.220	21.6[a]	19.4[a]
.357	1.320	21.49	212.0	66.19	3.107	3.220	22.9	20.8
.490	1.253	18.86	182.1	68.54	3.107	3.220	22.7	21.3
.759	1.108	14.99	141.3	71.75	3.107	3.220	21.6	21.2
.906	1.025	13.44	122.3	73.24	3.107	3.220	21.1	20.9
.952	0.998	13 01	115.5	73.77	3.107	3.220	21.0	20.7
.976	.984	12.79	112.8	73.99	3.107	3.220	21.0	20.6
1.000	.969	12 61	109.4	74.25	3.107	3.220	20.8	20.6
						Average	21.6	20.7

[a] Values below *a* in each series were used in obtaining averages.

TABLE III

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from Dimethylaniline

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g./sq. cm.	A_{12} silica	Adsorption Et_2CO_3 u mole/sq. cm. At silica interface	 At water interface	Area of molecules sq. cm. × 10^{16} At silica interface	 At water Interface
0.000	0.9519	25.81	224.2	65.32	...	...	..	..
.026	.9524	24.56	213.4	66.08	0.121	0.355	25.4	20.6
.052	.9529	23.78	208.0	66.51	.383	.492	22.3	22.2
.105	.9539	22.56	197.0	67.37	.638	.896	22.6	20.6
.208	.9558	20.50	179.4	68.75	.940	1.332	24.7	22.1
.311	.9575	19.01	165.8	69.82	1.174	1.606	25.1	22.4
.413	.9595	17.81	154.9	70.68	1.594	1.913	24.0	21.8
.515	.9613	16.69	144.1	71.53	1.594	2.236	24.7	21.5
.759	.9654	14.44	125.0	73.03	1.594	2.397	25.7	22.2
1.000	.9691	12.57	109.4	74.25	1.594	2.518	25.8	22.5
						Average	24.5	21.7

logarithm of the concentration of ethyl carbonate (in moles per cc.), a curve is obtained, for each solvent, which straightens out and approaches a constant slope as the concentration of ethyl carbonate increases. Since the adsorption of solute at any concentration is, according to the theorem, directly proportional to the slope of the curve at that point, it appears that "saturation" of the surface by adsorption must have been reached when this slope no longer changes. That is, from this point on the concentration of solute in the interfacial layer is in excess of the bulk concentration by a constant amount.

The calculated values for adsorption of ethyl carbonate by silica from each of the three solvents are given in the tables (column **6**). It is seen that at a silica surface ethyl carbonate is adsorbed from benzene to a somewhat greater extent than from alpha bromonaphthalene, while from dimethylaniline the adsorption is much less.

The values for adsorption of ethyl carbonate at a water interface from the same three solvents are also given in the tables (column 7). The adsorption values shown in this table were calculated by applying Gibbs' equation to interfacial tension concentration data. As in the case when silica was the adsorbent, adsorption is greatest from benzene and least from dimethylaniline—an observation which is in agreement with the widely accepted view that silica and water surfaces behave very similarly toward organic liquids.

Calculation of Area of Adsorbed Molecules.—It is of interest also to compare the calculated area of molecules adsorbed at a silica surface with the calculated area of the same molecules adsorbed at a water surface. Such results are summarized in the tables (columns 8 and 9). The method of calculation is one used by Bartell and Mack[5] which has been designated the "modified mixture law" method. It is assumed that if there were no adsorption the adhesion tension–concentration curve would be a straight line. To determine the concentration of solute in the interface corresponding to any given concentration in the bulk of the solution one needs simply to draw a horizontal line from the adhesion tension-concentration curve to the straight line joining the two ends of the curve. The concentration corresponding to the intersection of the two lines is the concentration of solute in the interfacial layer. This gives the value called "total" moles per cc. in the surface. The adsorption as shown in the previous tables is the excess moles per sq. cm. in the surface. The total moles per sq. cm. is obtained by adding to this quantity the value of $c^{2/3}/N^{1/3}$ in which c is the concentration (moles per cc.) in the solution and N is Avogadro's number. The term $(c^{2/3}/N^{1/3})$ is moles per sq. cm. in the bulk of the solution and when added to the excess moles per sq. cm. in the surface (adsorption) gives the total moles per sq. cm. in the surface. The thickness of the surface layer, then, is given by the quotient

$$t = \frac{\text{total moles/sq. cm.}}{\text{total moles/cc.}}$$

and the area of an adsorbed molecule by

$$a = \frac{M}{Ndt}$$

where d is the density and M the molecular weight.

Bartell and Mack showed empirically that for applying the mixture law method to calculations of this sort, it was more suitable to use volume fraction than mole fraction values in expressing solution concentrations

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(5) Bartell and Mack, *J. Phys. Chem.*, **36**, 65 (1932).

Consequently in obtaining the area values given in the tables mole fractions were converted to volume fractions and graphs were drawn from which the interfacial concentrations were determined.

The area of the ethyl carbonate molecule adsorbed on silica was found to be practically the same from the three different solvents, which indicates that the adsorption calculated by means of Gibbs' equation and adhesion tension data must be approximately correct. By an exactly analogous method the area of the ethyl carbonate molecule adsorbed at the water interface was calculated. (Column 9 in tables.) It had been previously demonstrated[5] that this method gives reliable values for the area of molecules adsorbed at liquid–liquid interfaces. The close agreement between the calculated area at the water interface and the calculated area at the silica interface is further evidence that the calculation of adsorption at solid surfaces from adhesion tension data is justified.

Summary

1. A method was developed for calculating adsorption at solid–liquid interfaces by means of the Gibbs adsorption theorem using adhesion tension data instead of surface tension or interfacial tension data.

2 Adhesion tension values against silica and interfacial tension values against water were determined for three binary liquid systems throughout the entire concentration range.

3. The order of "maximum" adsorption of a given solute from a series of three organic liquids was found to be the same whether silica or water was used as adsorbent. This is in agreement with previous observations concerning the similarity between a water surface and silica surface in their relation to organic liquids.

4. From the adsorption data and by means of the "modified" mixture law method the area of adsorbed ethyl carbonate molecules was calculated. Six values were obtained using three solvents and two adsorbents. The agreement of the values is remarkably good, justifying in large measure the use of adhesion tension data for calculating adsorption at the solid–liquid interface

ANN ARBOR, MICHIGAN

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

The Vapor Pressure of Crystalline Benzene and Cyclohexene[1]

BY V. R. DEITZ

In the course of an investigation concerning symmetry calculations for molecules it was necessary to know accurately the vapor pressure of benzene and cyclohexene in the crystalline state at various temperatures. In order to fill this need the Knudsen method of measuring vapor pressure was modified to fit the requirements of low temperature, and measurements were obtained of the vapor pressure of benzene and cyclohexene in the temperature range 165–200°K.

I. Apparatus

A. Temperature Control.—For temperature control a thermostat was used which was an adaptation from that of Andrews and Southard.[2] A block of aluminum was machined to fit into a standard liter Pyrex Dewar flask, evacuated to about 5-mm. pressure. It was non-magnetically wound with about 80 ohms of constantan resistance wire and contained in the center a 3-cm. hole to take the tube in which the diffusion cell was hung. It also was equipped with thermocouples placed on the inside and outside.

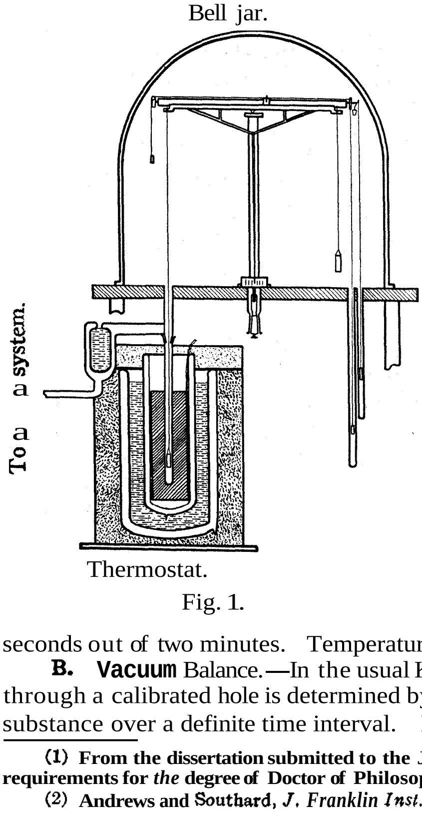

Fig. 1.

The Dewar containing the block was immersed in liquid air contained in a larger one-half gallon Dewar, see Fig. 1. After adjusting the necessary cork insulators, the assembly was raised into position by aid of an auto jack not shown in the figure.

The thermocouples functioned as follows: when the inside thermocouple showed that the temperature desired was being approached, the outside thermocouple current was opposed by the proper e. m. f. from a potentiometer circuit. Hence, when the temperature changed, the galvanometer placed in this circuit reflected a beam of light across a photoelectric cell. This regulation, properly amplified, tripped a relay which caused current to heat the aluminum block. Thus a balance between the cooling effect of the liquid air and the heating of the resistance coil produced a constant temperature. A period of about an hour was necessary before the temperature was constant. Under normal operating conditions, the heating current was on for about three seconds out of two minutes. Temperature control of ±0.05° was readily obtained.

B. Vacuum Balance.—In the usual Knudsen method the amount of vapor escaping through a calibrated hole is determined by noting the loss in weight of the evaporating substance over a definite time interval. Because of the difficulties incident to the low

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(1) From the dissertation submitted to the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Andrews and Southard, *J. Franklin Inst.*, **207**, 323 (1929).

temperature, it appeared advisable to follow the loss of weight continuously, without removing the diffusion cell from the thermostat.

A Becker analytical balance was mounted on a steel plate and equipped with devices so that it could be operated by controls outside of the vacuum chamber, see Fig. 1. The beam was lifted off and on the knife edges by replacing the usual eccentric mechanism by a screw device. The male screw was fastened to the vertical shaft of the balance release mechanism. The female screw had a flange midway up the side, so placed as to fit into a depression in the surrounding glass tube. The bottom of the female screw fitted snugly into the stopper part of a glass ground joint. This arrangement permitted the turning of the ground-glass stopper to rotate the screw which forced the central shaft up or down.

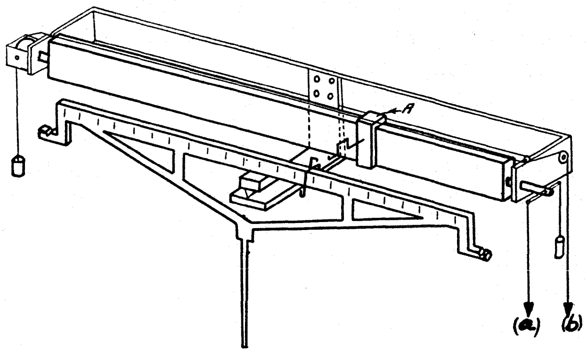

Fig. 2.—Rider adjustment.

A sufficiently heavy rider was used to measure a difference of 0.4 g. The rider was moved along by the mechanism shown in Fig. 2. The carriage A was pulled left or right by means of a solenoid arrangement. Once the carriage was pulled into place under the rider, the carriage was tilted by a second solenoid arrangement so as to pick up the rider. It was then moved into the desired position and lowered on the beam. The weighings were made by the method of swings. The usual index plate of twenty divisions was replaced by one of forty divisions, furnished by Christian Becker, Inc.. New York. The moving pointer was viewed through a telescope, so that the magnification allowed one to estimate tenths of division. Under the conditions and load of the experiment the sensitivity as determined several times averaged 2.05 ± 0.10 divisions per milligram

C. Diffusion Cell.—The substance was placed in a small brass cylinder, see Fig. 3. The platinum disk containing the calibrated hole was held between two thin lead gaskets, compressed by screwing down the top very firmly. The cylinder was threaded with 72 threads per inch. With these precautions, the amount of vapor escaping around the lead washers or down the threaded side was negligibly small.

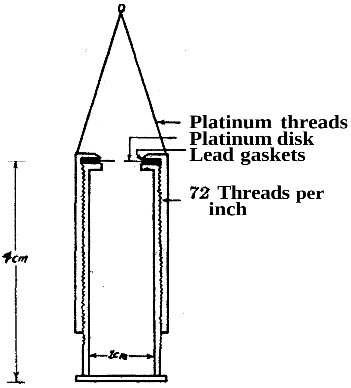

Fig. 3.—Brass diffusion

The freezing point curve of the benzene used in these experiments, after purification, showed the presence of not more than 0.1% impurity, the melting point being

+5.48°. The cyclohexene was purified by Dr. J. H. Bruun of the Bureau of Standards, to whom the author is very grateful. The cooling curve showed the presence of not more than 0.5% impurity; the melting point being −104.1°.

II. Procedure

The diffusion cell containing the substance was suspended from the balance arm and the glass tube put in place surrounding it, see Fig. 1. The system was slowly evacuated with the cell at a temperature of about −20°. This permitted the water vapor to be pumped off without undue loss of benzene. The temperature was then lowered to −78° and the steel mercury diffusion pump was started. After ten hours of pumping, liquid air was placed in the trap nearest the balance. Sublimation occurred then to this trap, instead of through the apparatus to the trap near the mercury pump. The thermostat was cooled in the meantime and quickly slipped into position. While the temperature slowly attained a constant value, the zero of the balance was kept on the scale by adjusting the rider. When the temperature appeared to be constant, readings were begun.

Since preliminary experiments indicated a temperature lag between the cell and the walls of the thermostat, the outside walls of the cell (not the top) were coated with a fine soot. A thermocouple was soldered to a thin copper cylinder which was also covered with soot and placed inside touching the walls and surrounding the cell. Under these conditions the temperature distribution was uniform. A conservative estimate places the temperature control above −100° at ±0.1° and for lower temperatures at 0.3°.

III. Results

It is, of course, necessary to know the total resistance to flow of the vapor from the diffusion cell to the liquid air surface. This was obtained by making several runs with benzophenone and comparing the results with the data of Volmer and Kirchhoff.[3] The value for the total resistance to the flow of the vapor was found to be 726 ± 20 units. There is an advantage in having the resistance at this high figure. In the work of Volmer

TABLE I

t, sec.	Change in scale divisions	Mass (mg.)	m = 1000 sec
900	1.2	0.60	0.65
780	1.1	.55	.70
660	0.95	.45	.70
630	.85	.40	.70
800	1.15	.55	.70
1300	1.9	.90	.70
850	1.15	.55	.65
			0.68 mg.

Hence $p = 7.12$ dynes

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[3] Volmer and Kirchhoff, Z. *physik.* Chem., 115, 233 (1926).

and Kirchhoff it was shown that for rapid diffusion of the vapor the surface is cooled quite appreciably. His results show that the values obtained for $w = 17.17$ were 18% lower than for values at $w = 205$. Table I illustrates the type of data obtained for benzene at $T = 195.0°K$.

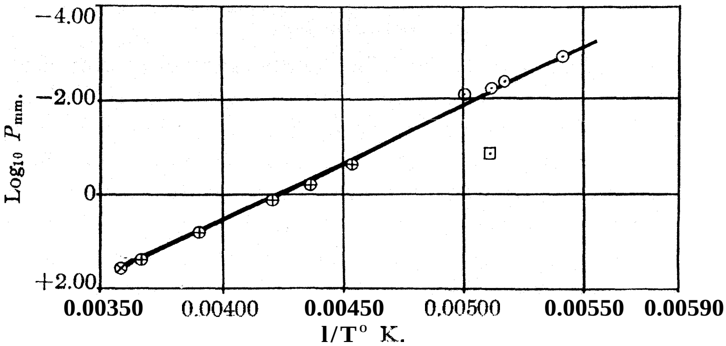

Fig. 4.—⊙, Deitz; ⊕, Mundel;[4] ⊗, Young and Fortey;[5] ⊡, Barker.[6]

Table II summarizes the direct results for benzene and for cyclohexene. The results for benzene are shown in Fig. 4, together with those of previous investigators.[4]

TABLE II

	Temp., °K.	Pressure, dynes
Benzene (s)	200.2	10.40
Benzene (s)	195.0	7.12
Benzene (s)	193.2	5.95
Benzene (s)	184.3	1.93
Cyclohexene (1)	176.2	3.75
Cyclohexene (s)	165.0	1.20

The author wishes to take this opportunity to express his sincere appreciation to Professor D. H. Andrews at whose suggestion this work was undertaken.

Summary

The vapor pressures of crystalline benzene and cyclohexene have been measured by means of a modified Knudsen procedure. An analysis of the experimental errors entailed leads to a probable error in the vapor pressure measurements of about 4%.

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(4) Mundel, *Z. physik. Chem.*, **71**, 235 (1910).

(5) Young and Fortey, J. *Chem. Soc.*, (London) **75**, 873 (1899).

(6) Barker, *Z. physik. Chem.*, *71*, 235 (1910).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. II. The Evaluations of Λ_0 and of K for Incompletely Dissociated Electrolytes

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

Assuming complete dissociation, the conductance of strong electrolytes in water (at low concentrations) as a function of concentration is well accounted for by the interionic attraction theory. Evidence is accumulating, however, which indicates that for all electrolytes in solvents of lower dielectric constant, as for weaker electrolytes in water, dissociation is incomplete at accessible concentrations. It has been proposed that a mass action effect be combined with the interionic effect[1] in order to account for the observed conductance values. This suggestion was first made by Davies[2] for various weak electrolytes in water and shortly afterward by Sherrill and Noyes[3] and by MacInnes.[4]

Later Onsager[5] derived an approximate conductance equation which took into account the mass action effect as well as interionic forces, and calculated several examples. An extrapolation method based on this equation has been applied by Davies[6] to non-aqueous solutions. Using a combination of the two effects, Martin[7] has computed conductance values for various salts in benzonitrile. The results obtained by the various writers indicate that a mass action effect must be taken into account, but the methods employed in evaluating the limiting conductance and the dissociation constant have been only approximate and it is difficult to determine how closely the experimental results may be accounted for by the assumptions made.

Perhaps the chief source of inconsistency lies in the value assumed for Λ_0, the limiting conductance of the electrolyte. In aqueous solutions, the value of Λ_0 for weak electrolytes may usually be evaluated from data relating to strong salts of the corresponding acid or base. In the case of solutions in solvents of lower dielectric constant, however, it is necessary to evaluate the limiting conductance for a given electrolyte from conductance data relating to that electrolyte alone. At present, only empirical extrapolation formulas have been employed for determining Λ_0 from conductance data which do not show the theoretical slope on a square root plot. For an exact comparison of theory and experiment, however, any

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(1) We are using the expression "interionic effect" in the sense of the theory of Debye and Huckel, although, of course, mass action likewise depends on an interaction of ions due to their changes, and depends upon the electrical properties of the medium

(2) Davies, J. *Phys. Chem.*, *29*, 977 (1925).

(3) Sherrill and Noyes, THIS JOURNAL, 48, 1861 (1926).

(4) MacInnes, *ibid.*, 48, 2068 (1926).

(5) Onsager, *Physik Z.*, **28**, 277 (1927)

(6) Davies, "Conductivity of Solutions," John Wiley and Sons, Inc , New York, 1930. Chapt. VII.

(7) Martin, J. *Chem. Soc.*, 3270 (1928).

empirical extrapolation function may be expected to lead to an error in the value of Λ_0. This, in turn, may induce a relatively large error in the value found for the dissociation constant K, since the error in $(1-\gamma)$ will be large if y, the fraction dissociated, is large, and the limiting form of the calculated curve may deviate greatly from the true curve. The difficulty may be overcome by solving the equations connecting conductance and concentration, which involve Λ_0 and the dissociation constant K. While these equations are not readily solved explicitly, they may **be** solved by successive approximation or by graphical means. Below is described a convenient method of solution and this method is applied to **a** variety of binary electrolytes in solvents of dielectric constant varying from 10.4 to 79. The calculated values are in agreement with the experimental values up to ion concentrations of approximately 2 X 10^{-3} *N*.

II. **The** Conductance Function

We consider a solution of a binary electrolyte AB and assume the usual equilibrium

$$A^+ + B \; ' \; A \; B \tag{1}$$

between ions and "undissociated molecules" of solute. It will not **be** necessary to consider the physical picture underlying (1); we shall accept the equation as implying that on the average a certain fraction of the total solute does not contribute to the transport of electricity through the solution during the conduction process. If the stoichiometric concentration is c, and the average fraction of solute free to carry the current is y, then the various concentrations are

$$[A^+] = [B'] = c\gamma$$
$$[AB] = c\,(1-\gamma)$$

where

$$\frac{1}{2}([A^+] + [B']) + [AB] = c$$

We assume as a first approximation that the thermodynamic properties and migration velocities of the ions depend on the total concentration of free ions 2 $c\gamma$ in the manner described by the equations of the interionic attraction theory. The changes in the properties of the solvent and in the distribution of ions in the "ionic atmospheres" which are caused by the presence of undissociated (non-conducting) ion pairs will be neglected. We shall also neglect higher terms[8] in the calculation of interionic effects. Finally, we assume that the undissociated molecules are present as a dilute solution in the classical sense. These assumptions appear to be justified at lower concentrations, even in solvents of quite low dielectric constant.[9]

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[8] Incidentally, we might mention that, since we limit our discussion to binary one-one salts the odd terms in the power series expansion used in computing interionic effects vanish, and that the valence factor $(z_1z_2)^n$ in the terms of this series always is unity.

[9] By "lower concentrations," we mean up to 0.003–0.004 N in liquid ammonia. for example. The only way to test the validity of the assumptions is to apply them to a practical case and see whether calculated results based on the assumptions agree with the observed experimentalfacts

The equilibrium function describing reaction (1) is then given by

$$\frac{[A^+]\, f_{A^+}\ [B]\, f_{B^-}}{[AB]\, f_{AB}} = K$$

where the activity coefficients are represented by f. Our assumption that the neutral molecules are present in dilute solution is equivalent to setting $f_{AB} = 1$. We shall employ Debye's first approximation to calculate these coefficients for the ions, using, in accordance with our assumptions, $2\,c\gamma$ for the total ion concentration. Then

$$-\log_{10} f = \beta \sqrt{c\gamma}/(1 + \delta \sqrt{c\gamma}) \qquad (2)$$

where

$$\beta = 0.4343 \frac{e^2}{2DkT} \left(\frac{8\pi N e^2}{1000\, DkT}\right)T' \qquad (2a)$$

and

$$\delta = \left(\frac{8\pi N e^2}{1000\, DkT}\right)^{1/2} a \qquad (2b)$$

Here,[10] e = the electronic charge = 4.770×10^{-10} e. s. u., N = Avogadro's number = 6.06×10^{23}, k = Boltzmann's constant = 1.371×10^{-16} erg/1°, D is the dielectric constant of the solvent, T is the absolute temperature, and a is the ionic radius.[11]

If we substitute our symbols for the concentrations, and assume $f_{A^+} = f_{B^-}$ the equilibrium equation becomes

$$c\gamma^2 f^2/(1 - \gamma) = K \qquad (3)$$

For convenience in later manipulation, we shall introduce a variable x defined by

$$x = (1 - \gamma)/\gamma^2 = cf^2/K \qquad (4)$$

For a solution containing $c\gamma/1000$ equivalents per cc. of anions and cations with mobilities v_{B^-} and v_{A^+}, respectively, the specific conductance κ is given by

$$1000\kappa = Fc\gamma(v_{A^+} + v_{B^-}) \qquad (5)$$

where F = 96,494 international coulombs per equivalent.[12] The equivalent conductance is defined as

$$\Lambda = 1000\ \kappa/c \qquad (6)$$

According to the interionic attraction theory, the mobilities vary linearly with the square root of the ion concentration; if we use Debye's equation to represent this change, we have, in view of (5) and (6)

$$A = \gamma(\Lambda_0 - \alpha \sqrt{c\gamma}) \qquad (7)$$

where Λ_0 is the limiting value of the equivalent conductance, and α has the value computed by Onsager

$$\alpha = \frac{8.18 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{82}{\eta(DT)^{1/2}} \qquad (8)$$

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(10) Birge, *Phys. Rev. Supplement*, **1**, *1* (1929).

(11) The value of a may be estimated from the limiting conductance by means of Stokes' law with sufficient accuracy to be used in a *correction* term,

(12) Ref. 10, p. 36.

Here η is the viscosity of the solvent and the other symbols have their usual meanings.

We now have a system of equations (2), (3) and (7) which implicitly describe the conductance curve

$$A = \Lambda(c)$$

Explicit solution in this form is difficult, due to the mixed form (transcendental, quadratic and cubic) of the system, but by means of the variable x, it is possible to transform the equations in such a way that calculation will be convenient. The explicit solution may be carried out in principle as follows: we regard c and A as known quantities from experiment, and may solve (7) in the form $\Lambda_0 = \Lambda_0(\gamma)$. From (3) and (3), we eliminate f and obtain $\gamma = \gamma(K, a)$, which, in view of the approximate relation between Λ_0 and a contained in Stokes' law, and the relative unimportance of the δ-correction term, may be written $\gamma = \gamma(K)$. From these two equations, we eliminate γ and obtain a relation between Λ_0 and K, $F(K, \Lambda_0) = 0$. We have as many equations (7) as we have experimental points $A = \Lambda(c)$. Corresponding to any two pairs of values of c and A, the equations $F_1(K, \Lambda_0) = 0$ and $F_2(K, \Lambda_0) = 0$ may be solved for K and Λ_0.

Before considering the general case, however, it is of interest to mention two limiting cases. If K is large, γ approaches very near to unity and (7) reduces first to Onsager's equation

$$\Lambda = \Lambda_0 - or\sqrt{c} - \Lambda_0 c/K \tag{9}$$

and, for K still larger, to the limiting law for complete dissociation

$$A = \Lambda_0 - \alpha\sqrt{c} \tag{10}$$

It should also be noted that, in any case, the limiting slope on a Λ–$\sqrt{c}$ plot is α. If, on the other hand, K is very small, (1– y) may be replaced by unity in (3), and a $\sqrt{c\gamma}$ becomes negligible compared to Λ_0, so that

$$\gamma \approx \Lambda/\Lambda_0 \tag{11}$$

and the equilibrium equation becomes

$$c\Lambda^2 = K\Lambda_0^2 \tag{12}$$

We should expect, therefore, that log A plotted against log c would be a straight line with slope

$$\frac{d \log A}{d \log c} \quad \frac{1}{2} = - - \tag{13}$$

when K is small. Also, if the limiting conductance is known, approximate values of K may be computed by (12).

In the general case, both the change of ion concentration and of ion mobility with concentration must be considered. If we rewrite equations (7) and (2) in terms of x, we obtain

$$\frac{A}{\Lambda_0} = \gamma - \frac{or\sqrt{K}}{A,}\,\frac{x^{1/2}\,\gamma^{3/2}}{f} \tag{14}$$

and

$$-\mathbf{flog}\, f = \beta\sqrt{K}\sqrt{x\gamma}/(1 + \delta\sqrt{c\gamma}) \tag{15}$$

By solving (4), we obtain

$$\sqrt{x} = \sqrt{1 - \gamma}/\gamma \qquad (16)$$

$$\gamma = (\sqrt{1 + 4x} - 1)/2x \qquad (17)$$

For small values of x, the power series

$$\gamma(x) = 1 - x + 2x^2 - 5x^3 + 14x^4 - 42x^5 + \dots \qquad (18)$$

may be used to calculate y from x.

The values of the limiting conductance Λ_0 and of the dissociation constant K are determined from conductance data as follows. An approximate[13] value γ' of γ is obtained simply by replacing y in the interionic attraction term of (7) by Λ/Λ_0

$$\gamma' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-3/2}\sqrt{c\Lambda}} \qquad (19)$$

The value of Λ_0 used here is obtained by any convenient method, such as a free-hand extrapolation of the experimental Λ–$\sqrt{c}$ curve; the final result is independent of the value of Λ_0 initially assumed. The approximation is repeated according to the scheme

$$\gamma'' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-1}\sqrt{c\gamma'}}, \text{ etc.}$$

which converges to a constant value. Having determined γ, $\sqrt{x}$ is computed from (16) and f from (2). The $\sqrt{x}$ is plotted against $f\sqrt{c}$. (The square root plot generally gives the more convenient scale.) According to (4), this plot should be a straight line with slope $\sqrt{K}$, ***passing through the origin.*** If the value of Λ_0 used in (19) is greater than the actual value of Λ_0, the $f\sqrt{c}$–$\sqrt{x}$ curve will have a positive intercept on the $\sqrt{x}$ axis. If this is the case, the computation is repeated for several smaller values of Λ_0, until a small negative intercept is obtained; the Λ_0 values used are then plotted against the corresponding $\sqrt{x}$ intercepts and a value is ***interpolated*** which gives a zero intercept. The value of $\sqrt{K}$ is determined by plotting the slopes of the $f\sqrt{c}$–$\sqrt{x}$ lines against the intercepts and interpolating as above. Since the $f\sqrt{c}$–$\sqrt{x}$ curve is very nearly linear (except in the extremely dilute region) even when the value of Λ_0 chosen is not the true value, it is sufficient to carry out the above calculation at only two concentrations which are taken in the range of concentration where the experimental error is small. This will give a value of Λ_0 which is as accurate as the two data; the computation may then be repeated with this value of Λ_0, using all of the experimental data, and weighting the points according to their accuracy if desired. If the $\sqrt{x}$ intercept thus determined is not quite zero, the values of Λ_0 and K may be corrected by means of the average slope of the interpolation plots. In our calculations we used at least five conductance determinations and, in this case, the interpolated

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(13) Equation (7) is cubic in $\gamma^{1/2}$ and may be solved by the usual algebraic methods or by the use of tables. In general, however, the convergent approximation method as here outlined is more rapidly handled.

values of Λ_0 and K needed no correction to bring them into agreement with the remaining data.

Figure 1 illustrates the application of the method to Kraus and Parker's[14] data for iodic acid in water. Curve I (scales above and left) covers the entire concentration range (0.0003–0.2 N) and corresponds to Λ_0 = 391.19; the three lower Curves II, III and IV (scales below and right), show the dilute region (0.0003–0.002 N) on a ten-fold magnified scale and correspond to Λ_0 = 390.8, 391.19 and 391.60, respectively. The points in the most dilute region are extremely sensitive to experimental error, because γ is greater than 0.99; nevertheless, it is obvious that Λ_0 = 391.60 is too great and Λ_0 = 390.8 is too small, because the average straight lines corresponding to these values definitely do not go through the origin, while the line for Λ_0 = 391.19 does satisfy this condition. Similar results have been obtained for about twenty-five electrolytes in various solvents.

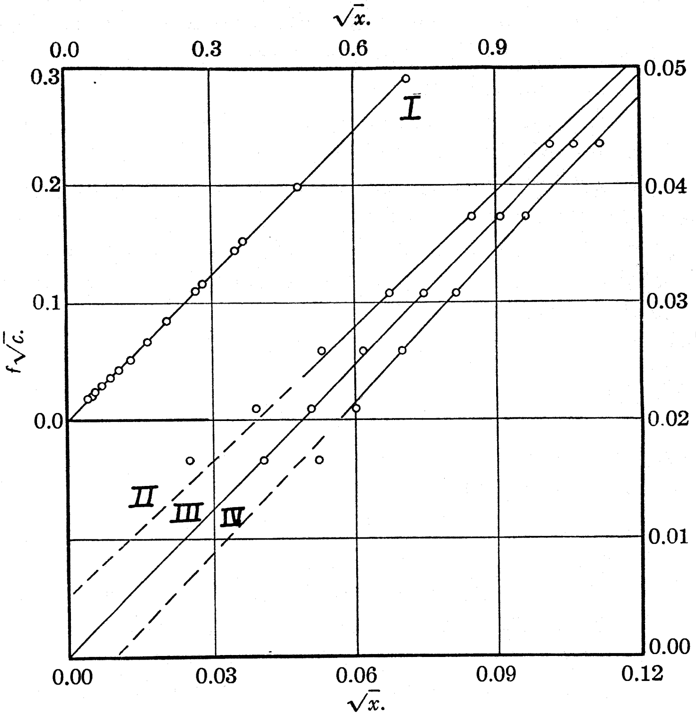

Fig. 1.—$f\sqrt{c}-\sqrt{x}$ plots for iodic acid in water.

The approximate linearity of the $f\sqrt{c}$–$\sqrt{x}$ plots, when the value of Λ_0 used above is near to the true value, is readily accounted for. The mass action equation (3) may be written

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[14] Kraus and Parker, THIS JOURNAL, 44, 2429 (1922).

$$f^2c\cdot\frac{\Lambda^2(1-\alpha\Lambda_0^{-1}\sqrt{c\gamma})^2}{1-\Lambda(1-\alpha\Lambda_0^{-1}\sqrt{c\gamma})/\Lambda_0}=K\Lambda_0^2$$

Now $f\sqrt{c}$ depends on the chosen value of Λ_0 through y in the expression for log f and hence is not very sensitive to changes in Λ_0. On the other hand, γ, and hence $\sqrt{x}$, depends directly on Λ/Λ_0, so that the main effect of changing Λ_0 is to change the values of $\sqrt{x}$. But, if Λ_0 is near to the true value, the left-hand side of the above function does not change much with c, so that $K\Lambda_0^2$ remains constant except for differences of higher order. For KA_0^2 constant, $f\sqrt{c}$ is linear against the square root of the reciprocal of the second factor on the left, which is the $\sqrt{x}$ value computed for the chosen value of Λ_0. The "true" value of Λ_0, however, is the value approached by A (observed) as c approaches zero, and this value obviously corresponds to the condition that $X = 0$ when c = 0.

If Λ_0 and K are known, the conductance curve may be computed as follows. A sufficiently dense set of values of $\sqrt{x}$ ranging from zero to $\sqrt{c_m/K}$ are listed, where c_m is the maximum concentration to **be** considered, and the corresponding values of y, $x^{1/2}$ y"'/' and $\sqrt{x\gamma}$ are read[15] from the graph (Fig. 2, Curves I, II and III). From a plot of —flog f against f (Curve IV, Fig. 2), approximate values f' off are determined according to the equation

$$-f'\log f' = \beta\sqrt{K}\sqrt{x\gamma}$$

With these values for f, approximate concentrations are computed from

$$\sqrt{c'} = \sqrt{K}\sqrt{x}/f'$$

and are used to determine the correction term in (15); then a second approximation f'' for f is obtained from

$$-f''\log f'' = \beta\sqrt{K}\sqrt{x\gamma}/(1+6\sqrt{c'\gamma})$$

This approximation scheme converges rapidly; when f becomes constant, $\sqrt{c}$ is given by (4). Then A is calculated according to (14) and a smooth curve is finally drawn through the computed (A, $\sqrt{c}$) points.

If it is desired to compute values of A for particular values of c, rather than to draw the conductance curve, a somewhat different procedure is followed. As a zeroth approximation, γ is set equal to unity in (2), and the corresponding value $(f^0)^2$ of f^2 is determined by

$$-\log(f^0)^2 = 2\beta\sqrt{c}/(1+\delta\sqrt{c})$$

The corresponding value x^0 of x is computed from the given concentration by means of (4), and then a first approximation y' for γ is obtained by substituting x^0 in (17) (or in (18) if x^0 is small). Then $(f')^2$ is computed from

$$-\log(f')^2 = 2\beta\sqrt{c\gamma'}/(1+\delta\sqrt{c\gamma'})$$

and the process repeated until y converges to a constant value. Then, with γ and f determined, A is computed according to (7).

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(15) For calculations requiring a higher accuracy than is permitted by a graph, a table of the values of $\sqrt{x}$, γ, $\sqrt{x\gamma}$ and $x^{1/2}$ $\gamma^{3/2}$ for round values of x is very convenient.

The general nature of the conductance function is evident from (14), where the conductance ratio Λ/Λ_0 is given as the difference between two terms, γ and $(\alpha\sqrt{K}/\Lambda_0)\ (x^{1/2}\gamma^{3/2}/f)$. The first represents the effect of mass action and the second the effect of interionic forces, corrected for incomplete dissociation. When the dissociation constant K is large, γ remains near unity and varies approximately as the *first power* of x, while the interionic attraction term has a large numerical coefficient and varies as the *square root* of x. Consequently, the variation of Λ/Λ_0 with c is governed primarily by the latter term, On the other hand, when K is small, even small concentrations soon correspond to large values of x where γ is decreasing rapidly (Curve I, Fig. 2). The interionic attraction term now has a small numerical coefficient and becomes merely a correction term to γ in determining Λ/Λ_0, since $x^{1/2}\gamma^{3/2}$ reaches a maximum at $x = 2$ (Curve II, Fig. 1). The decrease of f with increasing concentration increases the term in question, but the increase is retarded by the proportionality of f log f with $\sqrt{x\gamma}$. The various relations are illustrated by Fig. 2; if, for simplicity, we neglect the change of f with c, the conductance curve is simply the resultant of Curves I and II, where Curve I has the ordinate scale given in the figure and the scale for the Curve II is multiplied by $(\alpha\sqrt{K}/\Lambda_0)$. As might be expected, the conductance curves for weak electrolytes (*cf.* Fig. 3) markedly resemble the γ-curve of Fig. 2.

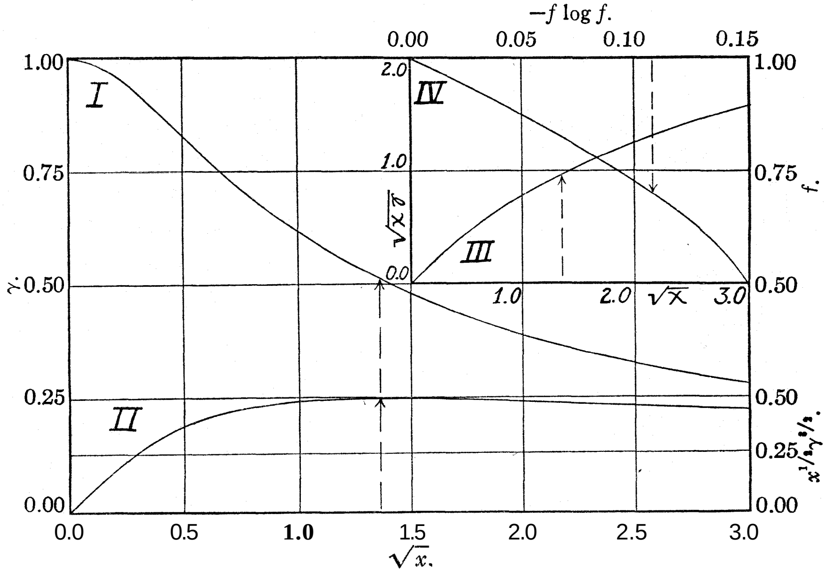

Fig. 2.—Functions involved in calculation of conductance.

The inflection point in the γ–$\sqrt{x}$ curve (I, Fig. 2) lies at

$$\sqrt{x} = \sqrt{\sqrt{3}/8} = 0.4653$$

and the corresponding concentration

$$c_{inf} = 0.2165\,K/f_{inf}^2 \qquad (20)$$

is proportional to the dissociation constant. A rough estimate of the concentration at which the inflection point appears may be obtained by setting f equal to unity. For example, if K is 5 X 10^{-4}, the inflection point in the $\gamma-\sqrt{x}$ curve appears in the neighborhood of 10^{-4} N, and one should not expect a $\Lambda-\sqrt{c}$ plot to have a slope equal to the limiting value at concentrations greater than 10^{-4} *N*. It is only at much lower concentrations that the interionic term becomes the controlling term, rather than a correction term to Λ/Λ_0. Incidentally, the presence of the inflection point accounts for the fact that many conductance curves are apparently linear in $\sqrt{c}$ over a certain range of concentration, but with a slope considerably greater than a.

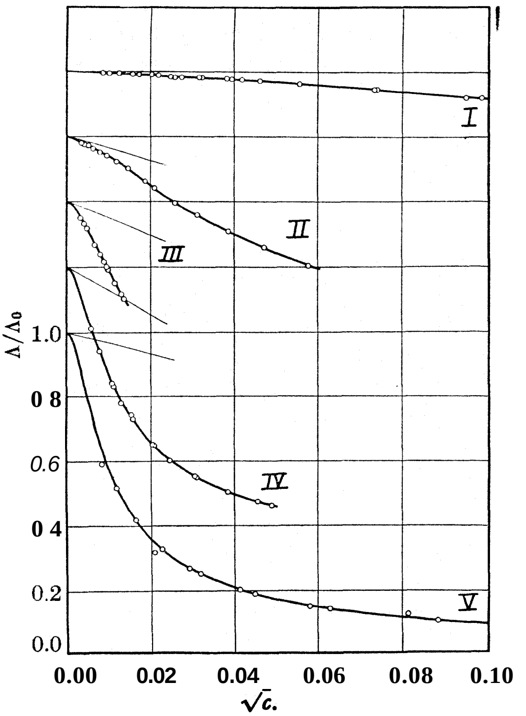

Fig. 3.—Comparison of calculated and observed conductance values: I. iodic acid in water; II, sodium bromate in ammonia; III, sodium iodide in amyl alcohol; IV, tetraisoamylammonium nitrate in ethylene dichloride; V, potassium amide in ammonia.

III. Comparison with Experiments

The method of computation presented above has been applied to a number of sets of conductance data, chosen to cover a fairly wide range of the specific constants involved. The results for several examples are shown in Fig. 3, where the conductance ratio Λ/Λ_0 is plotted against the square root of total concentration. (Each curve begins on the left at ($\sqrt{c} = 0$, $\Lambda/\Lambda_0 = 1$); in order to avoid confusion due to crossing curves, the different curves are displaced vertically. The ordinate unit is 0.2.) The circles indicate the various observed points. The curves are drawn according to equations (2), (3) and (7), where the constants have the values given in Table I, and the limiting tangents are drawn in accordance with (8).

A comparison of calculated and observed values for iodic acid in water is given in Table II. The specific conductance of the water used in Series

TABLE I
CONSTANTS FOR CONDUCTANCE CURVES

No.	Solvent	Solute	t, °C.	D	η	a
I	H_2O	HIO_3	25	78.57	0.00895	148.75
II	NH_3	$NaBrO_3$	−33.5	22.0	.00256	1052
III	$C_5H_{11}OH$	NaI	25	16.0	.038	59.19
IV	$C_2H_4Cl_2$	$(C_5H_{11})_4NNO_3$	25	10.4	.00785	500
V	NH_3	KNH_2	−33.5	22.0	.00256	1191

	δ	β	Λ_0	K
I	0.0153	0.5044	391.19	0.1686
II	1.54	4.742	286.2	.00253
III	2.80	5.517	11.246	.00295
IV	2.86	10.52	65.8	.00115
V	1.26	4.742	351.3	.000070

6 and 7 was about five times that used in Series 4 and 5; it will be noted that the agreement between calculated and observed conductances is much better for the former two than for the latter two series. Excepting the most dilute points in each of Series 6 and 7, the deviations are within the experimental error of several hundredths of 1% up to about 0.02 *N*;

TABLE II
CONDUCTANCE OF IODIC ACID IN WATER

$c \times 10^3$	Λ (obs.)	Λ (calcd.)	Δ, %	K
		Series 4		
0.068517	389.02	389.80	−0.19	...
.144572	388.94	389.08	− .03	...
.233308	388.31	388.40	− .02	...
.399158	387.46	387.35	+ .03	0.1938
.648686	386.12	386.01	+ .03	.1823
.986010	384.54	384.45	+ .02	.1764
1.49429	382.36	382.39	− .01	.1675
2.11108	380.06	380.16	− .02	.1646
		Series 5		
0.096291	389.02	389.52	−0.13	...
.168284	388.62	388.88	− .07	...
.286320	388.04	388.04	.00	0.1666
.465172	387.00	386.99	.00	.1729
.710642	385.76	385.71	+ .01	.1747
1.02335	384.31	384.29	.00	.1701
1.52809	382.26	382.26	.00	.1685
2.10323	380.09	380.18	− .02	.1648
		Series 6		
0.62349	384.97	386.14	−0.29	...
1.73067	380.92	381.51	− .15	...
3.00736	376.58	377.03	− .11	0.1562
5.38453	370.33	370.65	− .08	.1630
9.03267	362.15	362.28	− .03	.1669
16.1179	349.42	349.28	+ .03	.1698
30.5179	330.18	329.66	+ .12	.1715

TABLE II *(Concluded)*

Series 7

$c \times 10^3$	Λ (obs.)	Λ (calcd.)	Δ, %	K
1.43615	382.20	382.62	−0.10	0.1473
3.04044	376.77	377.15	− .09	.1580
5.47988	370.13	370.40	− .07	.1636
9.69682	360.79	360.91	− .03	.1672
18.3879	345.88	345.70	+ .04	.1698
34.9757	325.85	324.72	+ .28	.1748
67.3634	298.05	297.50	+ .14	.1707
193.258	244.36	245.22	− .21	.1658

beyond this concentration, the small differences increase with concentration. The maximum difference is 0.28%. The last column gives the values of K, calculated for each point.

Kraus and Parker, using the Ostwald dilution law for extrapolation, obtained $\Lambda_0 = 389.55$ and $K = 0.0717$; the present values are $\Lambda_0 = 391.19$ and $K = 0.1686$. Onsager[5] obtained $\Lambda_0 = 391.3$ and $K = 0.17$, which are in substantial agreement with our values. On the scale used, the curve for iodic acid (I, Fig. 2) shows little structure beyond the fact that it is slightly concave toward the concentration axis. Considering the high ionization of the acid, the value of K as calculated for the different points is remarkably constant; this is particularly true of Series 3 and 4. For $c = 4 \times 10^{-4}$ N, $\gamma = 0.998$, and here an error of 0.1% in Λ makes an error of 50% in $(1 - \gamma)$; K was therefore not calculated for the points in the most dilute region. The dissociation is too nearly complete to permit of accurate measurement of the undissociated fraction.

Sodium bromate in liquid ammonia (Curve II)[16] is a relatively much weaker electrolyte than iodic acid in water and, as might be expected from our discussion in the preceding section, gives a steeper conductance curve, which has an inflection point near 0.0003 N. Due to the lower dielectric constant and viscosity of ammonia compared to water, the slope of the limiting tangent for ammonia (Curves II and V) is greater than for water (Curve I), but on a $\Lambda-\sqrt{c}$ plot, the observed points and the calculated curve lie below the limiting tangent even at 10^{-5} N, the lowest concentration measured. Our present values for the constants of sodium bromate are $\Lambda_0 = 286.2$ and $K = 0.002532$. Kraus and Bray[17] obtained $\Lambda_0 = 278$ and $K = 0.0023$, based on the classical mass action equation. Davies[6] gives $\Lambda_0 = 281$ and $K = 0.0073$, using Onsager's approximate equation (9) for extrapolation. With dissociation constants as small as 10^{-3}, this simple parabolic equation may no longer be used (cf. (18)).

The curve for potassium amide[18] in liquid ammonia (V, Fig. 3) repre-

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(16) Paul B. Bien, Thesis, Brown University, 1932.

(17) Kraus and Bray, THIS JOURNAL, 35, 1337 (1913). These authors use the data of Franklin and Kraus, Am. *Chem.* J., 23, 277 (1900). The older data are in substantial agreement with the more recent values.

(18) Franklin, Z. *physik.* Chem , 69, 290 (1909).

sents a still weaker electrolyte. The shape of the curve recalls the curve for γ in Fig. 2 and, indeed, mass action controls the gross change of equivalent conductance for this salt. The interionic correction term, nevertheless, remains appreciable at all concentrations in the experimental range. If this correction is omitted and the simple mass action law is used for extrapolation, the resulting values are $\Lambda_0 = 301$ and $K = 1.20 \times 10^{-4}$, given by Kraus and Bray. These diverge widely from our present values: $\Lambda_0 = 351.3$ and $K = 0.700 \times 10^{-4}$. On the other hand, for a salt of this type, extrapolation by means of the simple square root law is impossible, since the approach to the limiting slope α does not appear at accessible concentrations.

Curve IV represents the conductance of tetraisoamylammonium nitrate[19] in ethylene dichloride, a solvent with dielectric constant 10.4. The corrections due to interionic effects are greater in this solvent than in ammonia because of its smaller dielectric constant.

The conductance of sodium iodide[20] in amyl alcohol is shown by Curve III. This solvent has a very high viscosity and a fairly low dielectric constant. The curve was not computed above the range of concentration covered by the data.

The examples described above cover a wide range of the various constants involved: dielectric constant 10.4–78.6; viscosity 0.038–0.00256; equivalent conductance 11.2–391; dissociation constant 0.00007–0.17. The agreement between calculated and observed values is in all cases satisfactory; we may therefore conclude that our assumptions are justified in the range of concentration considered, namely, up to ion concentrations of about 0.002 N.

Attention is called to a group of electrolytes whose behavior is incompatible with the equations here used to describe the conductance of weak electrolytes. A large group of strong electrolytes in water (for example, hydrochloric acid, potassium hydroxide, potassium chloride, etc.) give conductance curves which approach the limiting tangent from above, while a mass action effect causes the curves to fall below the limiting tangent. Apparently, some effect is here coming into play, which either is not taken into account in our equations or has been excluded by our assumptions. This behavior, *i. e.*, observed conductance greater than that calculated from our equations, is not limited to aqueous solutions, for most of the electrolytes which we have examined show positive deviations at higher concentrations (greater than about 0.01 N). In solvents of lower dielectric constant, the conductance curve generally exhibits a minimum. This increase of conductance with concentration at higher concentrations may be analogous to the effect observed in water, which has a very high dielectric constant.

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[19] Kraus and Fuoss, THIS JOURNAL, 55, 21 (1933).

[20] Kraus and Bishop. *ibid*. 44, 2206 (1922).

Summary

1. An exact method of solving the conductance equations for incompletely dissociated binary electrolytes is presented.

2. A method is described for determining the limiting equivalent conductance and the dissociation constant.

3. Five examples of application of the method are given, in which the constants of solvent and of electrolyte vary as widely as possible. Calculated and observed conductance values agree within the limit of experimental error up to ion concentrations of several thousandths normal.

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The Reaction between Osmium Tetroxide and Hydrobromic Acid. I. Equilibrium Study

BY H. DARWIN KIRSCHMAN AND WILLIAM R. CROWELL

Introduction

A study of the catalytic influence of ruthenium compounds on the decomposition of perchloric acid by hydrobromic acid recently made[1] has led to a similar investigation of the catalytic effect of osmium compounds on this reaction. This work is now under way. Since under certain conditions there is an appreciable action between the hydrobromic acid and octavalent osmium, it became necessary to study the latter effect separately.

The products of the reaction were found to be bromine (largely in the form of tribromide ion) and some form of osmium in a lower valence state. Data obtained in an examination of the reaction rate indicated that a state of equilibrium was reached. In the present paper are presented the results of a study of this equilibrium, together with possible interpretations of the results and an attempt to derive an equilibrium constant at 100°.

Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of bromine, octavalent and quadrivalent osmium.[2] The materials and their preparation have been described in the articles mentioned. In the present work, however, the bromine solution was 1.00 N in hydrobromic acid since it was found that the stability of the solution was much greater than in one-tenth normal acid as previously used, the concentration of the bromine solution in the stronger acid remaining unchanged for a period of

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(1) Crowell, Yost and Carter, THIS JOURNAL, 61, 786 (1929).

(2) (a) Crowell and Kirschman, *ibid.*, 51, 175 (1929); (b) 51, 1695 (1929); (c) Crowell, *ibid.*, 64. 1324 (1932).

several weeks. The quadrivalent osmium solution was made **2.40** *N* in hydrobromic acid since this concentration was most convenient in the preparation of the reaction tubes.

Experimental Procedure

In obtaining the experimental data the equilibrium was approached from both directions using different concentrations of the reacting constituents. From the direct side the initial reactants were octavalent osmium and hydrobromic acid in solutions of the two alone and in solutions of the two containing initially added amounts of bromine. From the reverse side the initial reactants were quadrivalent osmium and bromine in solutions of hydrobromic acid alone and in the acid solutions containing initially added amounts of potassium bromide.

The method of filling the reaction tubes and analyzing their contents was essentially the same as that described in our previous article.[2c] The various constituents were pipetted into Pyrex test-tubes, using such volumes as to secure the desired initial concentrations and a total volume of 10.0 cc. The tubes were sealed and heated in a water-bath at 100° for three or four days. At the end of that time the tubes were chilled in an ice-bath, broken in about 200 cc. of ice water and titrated with hydrazine sulfate solution. During the process of dilution and titration, the bromine was reduced to bromide and any Os_7 or Os_6 present was reduced to Os_4. Since it was impracticable to distinguish between the bromine and the reduced osmium in the hydrazine titration, it has been termed "total bromine titration." From the initial concentrations of osmium and bromine (in the cases where initial amounts were present) and from the results of the "total bromine titration" the concentrations of Os_8 and of reduced osmium can be calculated. In order to calculate the equilibrium concentration of bromine, it is necessary to know the valence state of the reduced osmium. The method of determining this is explained in the next section.

In Table I are recorded the data on the equilibrium experiments and the results of determinations of the "total bromine" in the reaction tubes. In columns 2, 3, 4 and 5 are shown the original concentrations of acid, bromine, octavalent and quadrivalent osmium in mols per liter at 25°. In column 6 appears the concentration of "total bromine" in mols per liter at 25° as determined by potentiometric titration with hydrazine sulfate. For each run these results represent the average value obtained in the titration of three or four tubes. The data in columns 3, 4, 5 and 6 enable us to calculate the equilibrium concentrations of bromine, octavalent and reduced osmium which are shown in columns 7, 8 and 9. The method of calculating these values will be explained in the next section in connection with the presentation of the proposed reactions.

TABLE I

RESULTS OF TITRATION OF BROMINE IN THE REACTION TUBES

	Initial concentration m./l. at 25°				Total Br_2[a] titration	Equilibrium conc. m./l. × 10^3 at 25°			$\frac{Os_7 \times Br_3^{-1/2}}{Os_8} = K_I$
Run	HBr	Br_3^- × 10^3	Os_8 × 10^3	Os_4 × 10^3	m./l. × 10^3	Br_3^-	Os_8	Os_7	
1	0.800	8.22	0.00	4.00	0.78	0.37	3.72	0.28	0.046
2	1.20	8.24	0.00	4.00	1.80	0.62	3.22	0.78	0.191
3	1.60	0.00	4.04	0.00	3.00	0.76	2.53	1.51	0.520
4	1.60	8.22	0.00	4.00	3.20	0.96	2.51	1.49	0.581
5	1.60	0.00	8.22	0.00	6.75	1.69	4.84	3.38	0.907
6	1.60	0.00	7.70	0.00	6.75	1.69	4.32	3.38	1.02
7	1.60	15.44	0.00	7.74	6.34	1.55	4.55	3.19	0.873
8	2.00	0.00	4.11	0.00	4.35	1.09	1.93	2.18	1.18
9	2.00	0.00	3.80	0.00	4.03	1.01	1.78	2.02	1.14
10	2.00	8.23	0.00	4.00	4.17	1.21	2.03	1.97	1.07
11	2.00	0.00	8.22	0.00	7.70	1.93	4.37	3.85	1.23
12	2.00	0.00	7.70	0.00	7.35	1.84	4.02	3.68	1.24
13	2.00	15.44	0.00	7.74	7.38	1.81	4.03	3.71	1.24
14	2.40	0.00	3.86	0.00	5.27	1.32	1.22	2.64	2.48
15	2.40	0.00	3.68	0.00	5.02	1.26	1.17	2.51	2.40
16	2.40	0.00	3.75	0.00	4.92	1.23	1.29	2.46	2.12
17	2.40	10.24	0.00	3.95	7.46	3.62	1.39	2.56	3.50
18	2.40	0.00	7.67	0.00	8.59	2.15	3.37	4.30	1.87
19	2.40	0.00	7.57	0.00	8.37	2.09	3.38	4.19	1.79
20	2.40	8.06	3.69	0.00	12.16	9.08	1.64	2.05	3.77
21	2.40	10.26	3.86	0.00	14.70	11.37	1.64	2.22	4.56
22	2.40	7.33	7.60	0.00	16.33	9.58	3.10	4.50	4.50
23	2.40	20.44	0.00	3.95	17.06	13.67	1.69	2.26	4.95
24	2.40	14.65	7.60	0.00	23.31	16.81	3.27	4.33	5.43
25	2.40	39.69	3.75	0.00	42.95	40.50	2.12	1.63	4.89
26	2.40	51.42	0.00	3.95	46.88	44.36	2.27	1.68	4.92
27	2.40	51.47	3.86	0.00	54.83	52.31	2.18	1.68	5.57
28	3.20	0.00	3.79	0.00	7.03	1.76	0.270	3.52	17.3
29	3.20	0.00	7.60	0.00	14.00	3.50	0.598	7.00	21.9
30	3.20	0.00	7.70	0.00	14.42	3.61	0.488	7.21	28.1
31	3.20	15.43	0.00	7.73	14.36	3.56	0.534	7.20	25.5
32	3.20	7.62	3.79	0.00	14.52	9.34	0.341	3.45	30.9
33	3.20	15.36	7.58	0.00	28.70	18.69	0.910	6.67	31.7
34	3.20	38.52	7.57	0.00	51.00	41.64	1.33	6.24	30.2

[a] From hydrazine sulfate titration of contents of reaction tube.

Derivation of the Equilibrium Constant

In runs 20 to 27 inclusive, in which the acid concentration was constant at 2.40 *N* and in which the total concentration of tribromide was high enough to be of the same order of magnitude as its equilibrium value, the functional relation of the tribromide concentration in the equilibrium expression was calculated on the assumption that the two forms of osmium appeared as the first power of their concentrations

$$\frac{\mathrm{Os}_{\mathrm{reduced}}}{\mathrm{Os}_8} \times (\mathrm{Br}_3^-)^m = K_{\mathrm{I}}$$

The data indicated clearly that m was approximately 0.50. Similar treatment of runs 32 to 34 inclusive, in which the acid concentration was 3.20 N, gave a like value for m.

In order to determine the effect of the activity of the hydrobromic acid upon the equilibrium an attempt was made to estimate the values of the activities of the hydrobromic acid at the different concentrations used and to determine the approximate value of n in the expression

$$\frac{\mathrm{Os}_{\mathrm{reduced}}}{\mathrm{Os}_8} \times \frac{(\mathrm{Br}_3^-)^{1/2}}{(\mathrm{HBr})^n} = K$$

The values of the mean ion activity coefficients of hydrobromic acid at 25° were estimated from the data of Bates and Kirschman[3] and of Livingston.[4] There was a considerable gap between the minimum values calculated from the vapor pressure measurements of the former and those obtained from the electromotive force measurements of the latter. In order to determine the coefficients in the working range of our experiments it was necessary to plot the two sets of data and extend the curves until a single one was obtained. To convert the vapor pressure results into activity coefficients the free energy data of Lewis and Randall[5] were used. The activity coefficients at 100° (the temperature of the reaction tubes) were then calculated by the use of the heat data given in the "International Critical Tables."[6]

The solution of simultaneous equations containing different values for the activities of hydrobromic acid and different concentrations of octavalent osmium, reduced osmium and of bromine showed n, the power of the hydrobromic acid activity, to be about four.

A reaction scheme which would require a value of one-half for m and approximately four for n seemed to be one of the following.

(1) A single reaction of the type

$$\mathrm{OsO_4 + H^+ + 5/2\ Br^- = Os(OH)O_3Br^- + {}^1/_2Br_3^-}$$

(2) A pair of reactions, the first of which is very rapid, producing a complex with a coördination number of eight and the second of which is the slower and equilibrium-determining step

$$\mathrm{OsO_4 + 7HBr = Os(OH)Br_7 + 3H_2O}$$
$$\mathrm{Os(OH)Br_7 + H^+ + 5/2\ Br^- = OsBr_8^- + {}^1/_2Br_3^- + H_2O}$$

In accordance with these proposed reactions it is assumed that septivalent osmium and tribromide ion are the products of the reduction of the octavalent osmium. The presence of septivalent osmium seems to be the most reasonable assumption to make in order that the tribromide-ion concentration appear in the equilibrium expression to the one-half power.

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(3) Bates and Kirschman, THIS JOURNAL, 41, 1991 (1919).

(4) Livingston, *ibid.*, 48, 45 (1926).

(5) Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, Chapt. 36.

(6) "International Critical Tables," Vol. V, p. 177.

In preliminary calculations of equilibrium constants using different exponents for the hydrogen and bromide ion activities, the best agreement was obtained when the combined exponent was 3.5 and that of the hydrogen ion was unity. Both in the cases where it was assumed that hydrogen ion had no part in the reaction and in those in which it was assumed that it appeared as the second power, non-concordant constants were obtained. In order to satisfy these requirements the presence of $Os(OH)Br_7$ and of $OsBr_8^-$ are not necessarily the only forms that might be postulated in scheme (2). Such octavalent forms as those ranging in composition from $OsO_3(OH)Br$ to $Os(OH)Br_7$ and such septivalent forms as those ranging in composition from $OsO_3(OH)Br^-$ to $OsBr_8^-$ might also be possible.

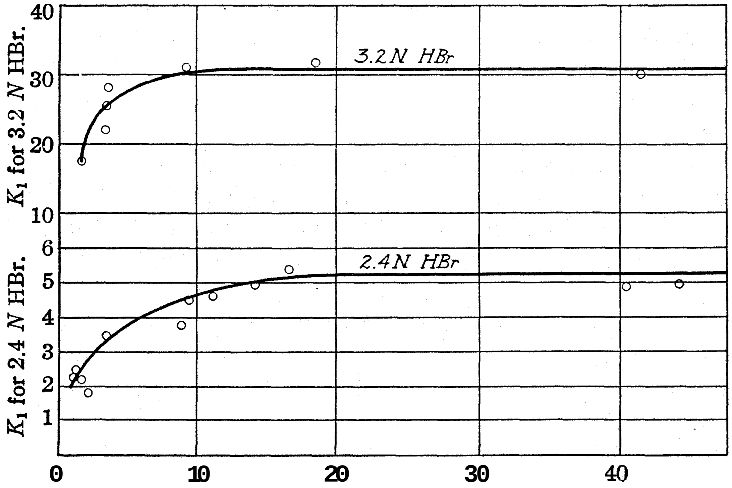

Fig. 1.

The results shown in columns 7, 8 and 9 of Table I were calculated under the assumption that the osmium in the equilibrium mixtures is reduced to a septivalent form and that during the titration with hydrazine sulfate it is further reduced to a quadrivalent form with the liberation of three equivalents of bromine per mol of osmium reduced. Consequently a correction amounting to one and one-half times the molar concentration of the reduced osmium was deducted from the titrated value of the bromine (in column 6) in order to obtain the equilibrium concentration of the tribromide ion. In column 10 are the calculated values of K_I using the equilibrium concentrations of Os_7, Os_8 and of Br_3^- expressed in millimoles per liter at 25°. It was noted that in the runs at 2.4 and 3.2 N in which the bromine and osmium concentrations were varied over a wide range, the constants seemed to depend upon the concentration of bromine present. Accordingly, the values of K_I were plotted against bromine concentrations at equilibrium and the curves shown in Fig. 1 were obtained. It will be seen that at the lower bromine concentrations the constants are also lower, but with increasing concentration of bromine they increase and reach a constant value. The values corresponding to the horizontal portion of the curves were used in the final calculation of the equilibrium constants. In the runs at other acid concentrations the average values for the constant K_I were used.

If the activity coefficient of the osmium tetxoxide is assumed to be unity and that of the septivalent osmium and the tribromide ion assumed to be equal to the mean ion activity coefficient of the hydrobromic acid, we may write for the equilibrium constant in either of the above cases

$$\frac{(\mathrm{Os}_7^-)(\mathrm{Br}_3^-)^{1/2}\,\gamma_\pm^{3/2}}{(\mathrm{Os}_8)(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_\pm^{7/2}} = K = \frac{K_I \times g^{-0.5}}{(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_\pm^{2}}$$

where Os_7^-, Br_3^-, Os_8, H^+ and Br^- represent the concentrations of these substances in mols per thousand grams of water, g the number of grams of water per liter of solution at 25°, $\gamma_\pm$ the mean ion activity coefficient of the hydrobromic acid at 100°, and K the equilibrium constant at 100° when the concentrations of all the constituents are expressed in mols per thousand grams of water.

In Table II are given the average values of the equilibrium constants as calculated according to the above expression. The results for experiments in which potassium bromide and hydrobromic acid were used are shown in runs 37–41, inclusive. As the literature does not contain data on the activity coefficients of hydrobromic acid in solutions of potassium bromide at the concentrations used in our work, these values at 25° were estimated by use of the results of Harned[7] on the activity coefficients of hydrochloric

TABLE II

CALCULATION OF EQUILIBRIUM CONSTANTS AT 100°

Runs	Concentration in mols per 1000 g. of water HBr	KBr	K_I	g	Log $\gamma_\pm^2$ at 100°	K X 10^6
1	0.825		0.0450	977	2.7390	5.2
2	1.24		0.192	967	2.8143	4.5
3– 6 incl	1.66		0.780	958	2 9544	4 8
8–13 incl.	2.10		1.20	954	3.0443	2.6
14–27 incl.	2.55		5.30[a]	945	3.1917	4.2
28–34 incl.	3.50		31.0[a]	916	3 5343	3.7
			Average of all HBr runs except 8–13			4 5
37	1.26	0 84	0 846	952	2.7677	5 8
38	1.70	0.85	1 30	940	2.8151	3.7
39	2.14	0.86	1.87	934	2.8572	2.6
40	2.62	0.88	3.96	915	2.8471	3.1
41	1.75	1.75	5.96	915	2.9280	5.8

[a] These values were taken from the curves of Fig. 1. The remaining values are averages.

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(7) Harned, THIS JOURNAL, 48, 429 (1926)

acid in solutions of potassium chloride. The coefficients at 100° were calculated by use of the conversion factors employed in the salt-free hydrobromic acid runs. The density–percentage composition data required to convert mols per liter into moles per 1000 g. of water were obtained from the "International Critical Tables."[8]

Since in the absence of direct data on the activity coefficients of the constituents involved it has been necessary to make certain assumptions concerning these coefficients in the calculation of the equilibrium constants; no doubt the latter will be modified to some extent when these data are obtained. The agreement of our results among themselves in most cases is surprising. In a qualitative way, at least, they indicate that at low concentrations of acid and of osmium and at high tribromide concentrations the tendency is for the osmium to be reduced to the septivalent form. At higher acidities and lower tribromide concentrations it is possible that other lower valence forms of osmium, such as sexivalent and quadrivalent compounds, are also present. Due to the instability of the osmium compounds present in the equilibrium mixture, we have not yet been able to isolate them in the original state. It might be recalled in this connection that in the potentiometric titration of octavalent osmium with titanous chloride in hydrobromic acid solutions a double inflection in the curve was obtained when the determination was made at 25° (Ref. 2a, p. 1697). This behavior was not explained at the time but it might be due to the presence of septivalent osmium whose reduction potential might be very near that of octavalent osmium but whose rate of reduction might be somewhat slower.

The color changes of the solutions do not afford much help in the interpretation of results, although at the lower acid concentrations the shade is more toward a brownish-red, while in the more concentrated acid solutions the color is a deeper red. Quadrivalent osmium formed in concentrated hydrobromic acid solutions produces crimson colored solutions and it may be that the deep red color of the equilibrium mixture at the higher acidities is due to the presence of small amounts of the quadrivalent form.

The results of the experiments in which hydrogen bromide and potassium bromide were used show clearly that the hydrogen and bromide ions each have their separate effects upon the equilibrium. Because the method of estimating the activity coefficients in these runs involved greater approximations than in the runs in which potassium bromide was absent, the individual equilibrium constants were not considered in obtaining the final average value. The agreement with the other values, however, is probably as good as could be expected.

In the experiments with 2.00 N hydrobromic acid the constants are much lower than in the runs at lower acidities but are of the same order of magni-

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(8) "International Critical Tables," Vol. III, pp. 55 and 87.

tude as those for 1.60, 2.40 and **3.20** N acid at low tribromide concentrations. This is probably due to the low concentrations of tribromide in all the runs at 2.00 N acid and to the tendency to form lower valence compounds of osmium at this acid concentration. For these reasons, this constant was also omitted in the calculation of an average value. Using 4.5×10^{-6} for the constant, calculations of the ratios of concentrations of octavalent to septivalent osmium in solutions 0.10 and 8.0 *N* in hydrobromic acid containing equivalent amounts of tribromide ion are in agreement with previous statements[2c] that the conversion of octavalent into reduced osmium in 8.0 normal acid is practically complete and that the reverse reaction is likewise practically complete in 0.1 normal acid.

In conclusion, we take this opportunity to thank Dr. Don M. Yost for the very many helpful suggestions made during the course of this work.

Summary

A study of the equilibrium involved when octavalent osmium reacts with hydrobromic acid in a closed tube at 100° with the formation of bromine and lower oxidation states of osmium has been made. The results indicate that at low concentrations of osmium and of acid and high bromine concentrations the osmium was reduced to the septivalent form.

The mass action expression was found to have the form

$$\frac{(\mathrm{Os}_7^-)(\mathrm{Br}_3^-)^{1/2}}{(\mathrm{Os}_8)(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_\pm^2} = K$$

where $\gamma_\pm$ represents the mean ion activity coefficient of the hydrobromic acid; and on the basis of this expression two possible types of reactions were suggested.

The average value for the equilibrium constant K when the concentrations are expressed in moles per 1000 grams of water is 4.5×10^{-6}.

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The Effect of Crystal Symmetry and Chemical Composition on the Energy Levels of Solids

BY F. H. SPEDDING[1] AND G. C. NUTTING

In the past few years energy level diagrams have been constructed for most of the gaseous atoms and the more simple gaseous molecules and many relations have been established between the physical and chemical properties of the substances investigated and their energy levels.

As a large part of chemistry deals with solids and solutions it would be very desirable to extend these relations so as to apply to them. Unfortunately, however, very little at present is known about energy levels in solids.

So far the two most promising methods of attack on this problem have been by means of the double crystal x-ray spectrograph and the Raman effect. Both these methods have serious disadvantages. The former deals with spectra in the x-ray region where the energies involved are very large and differences due to chemical causes are hard to measure with any great accuracy as they are only a small percentage of the total energies concerned. In the part of the spectrum ordinarily investigated 15,000 calories correspond to a shift of only 0.1 to 0.01 x-units or about 0.0001 to 0.00001 of the total energies involved. On the other hand, while the Raman effect is free from this objection, it gives only a few lines at most and an energy level diagram without additional help is out of the question.

Another method of investigation[2] which gives great promise but which so far has not produced many quantitative results is the study of the absorption spectra of solids and solutions or glasses particularly at low temperatures. This method is free from the objections raised but unfortunately most of the lines arising from the energy levels are blurred into broad diffuse bands in most of the solids and solutions investigated due to the temperature agitation. The energy levels are non-degenerate due to the electric fields of the neighboring atoms or ions and the amount these levels are split apart depends on the strength of the fields, which at room temperatures are fluctuating very rapidly as the nearby atoms approach and recede from the atoms in question. Since the photographic plate indicates the differences between sets of levels over an interval of time the net effect is the blurred bands observed.

It is probably true also that many of the higher excited states in the free atom tend to become unstable upon the close approach of another atom

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(1) National Research Fellow in Chemistry.

(2) This subject has received a great deal of attention but usually with the emphasis on other phases than the energy levels. A few investigators who have done considerable work in the field are J. Becquerel, *Leiden* Communications; R. Brunetti, *Il Nuovo Cimento;* P.F Ephrain, *Berichte;* Jones and Strong, *Carnegie* Pub.; Freed and Spedding, *Physical* Review

and an electron which ordinarily would jump to a well-defined level giving rise to a sharp line will move into the unstable region and a continuum will result. This is not true for all states so by cooling the solids or glasses to very low temperatures it is possible to resolve into sharp lines the bands from a large number of compounds.

The absorption spectra of the rare earths offer the most encouraging points of attack upon the problem of the energy levels of solids. The reason for this becomes evident upon examination of their electronic structures.

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
La^{+++}	2	2	6	2	6	10	2	6	10	..	2	6
Ce^{+++}	2	2	6	2	6	10	2	6	10	1	2	6
Pr^{+++}	2	2	6	2	6	10	2	6	10	2	2	6
Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6
Lu^{+++}	2	2	6	2	6	10	2	6	10	14	2	6

It is seen that the "active[H3] electrons are in the 4f shell and that they are partially shielded from the effects of the neighboring atoms by the completed 5s and 5p shells. These electrons, then, are not nearly so much disturbed as are the active electrons in iron or chromium, where they are not so shielded.

One might expect that the energy levels in a solid would be intermediate in type between those of a gaseous atom and those of a gaseous molecule. To a first approximation, in a gaseous atom the electric field is spherically symmetrical about the nucleus. In a diatomic molecule it is cylindrically symmetrical around the line joining the nuclei. In a polyatomic molecule the symmetry varies widely, but it is apt to be very low.[4,5]

Because of the regularity of the crystal lattice the electric symmetry in a solid is probably higher and in the case of the cubic lattice the levels are much more likely to be similar to atomic than molecular levels. It is to be expected that the fields are of various strengths, some of which make the atomic levels non-degenerate as would weak Stark fields, while others destroy the coupling between the electrons and correspond to strong Stark fields.[6]

The basic levels of the rare earths are atomic, for Hund[7] has shown that the measured magnetic susceptibilities of the rare earth ions in the solid state are those to be anticipated if the lowest levels in the solid and the gas

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(3) An "active" electron is one which is excited by the light absorbed. The electrons in the completed shells are firmly coupled to give a ^1S term in which the resultant orbital and spin moments are zero. A considerable amount of energy is required to break this coupling

(4) The effect of the electric fields is to make the atomic levels non-degenerate, just as an externally applied electric field produces Stark splitting. When the field is weak it couples with the j of an atomic term, thus splitting the level into a number of components. When it becomes strong it breaks down the coupling between spin and orbital moments themselves. In fields of the higher degrees of symmetry there is partial balancing of forces which tends to diminish the splitting.

(5) Robert S. Mulliken gives an excellent account of this effect in his "Interpretation of Band Spectra," *Rev.* Modern *Phys.*, 4, 1 (1932).

(6) This effect has been discussed by H Bethe, Ann. *Physik,* 3, 133 (1929), from the standpoint of wave mechanics and group theory.

(7) Hnnd, *Z Physik,* **33**, *855* (1926)

are the same. The rare earths offer the further advantage that they give an unusually large number of lines in the photographic region of the spectrum. This is probably due to the fact that while the orbits just outside the completed shells are greatly influenced by the neighboring atoms, they are less influenced than those orbits further out, and electronic states arising from them will have more of their levels potentially stable. Thus in the rare earths electronic transitions occur to levels which in other atoms would correspond to the basic levels.[8]

It is possible also that in strong electric fields of the crystal quadripole radiation may be permitted and jumps take place by a recoupling of the 4f electrons.

This is the first of a series of papers on a systematic investigation of the energy levels of solids and gives in detail the results reported briefly in a letter to the *Physical Review* of December 15, 1931.

Experimental

Gadolinium salts are the most desirable for this sort of work. Gd^{+++} ion gives sharp lines at room temperature; it shows the simplest absorption spectra of all the rare earth ions, its lines and multiplets being well separated from one another, and its basic level $^8S_{7/2}$ is known to be single. Its chief disadvantage is that most of its lines occur in the ultraviolet. The gadolinium material used was from two sources. One, of almost atomic weight purity, was furnished us by Professor B. S. Hopkins of the University of Illinois The other was from the Welsbach Company and contained about 1% Tb and 0.5% Sm.

Crystallographic measurements were made for us by Professor Adolph Pabst of the Mineralogy Department of the University of California and we wish to express our thanks for this assistance.

$GdCl_3 \cdot 6H_2O$.—The spectrum of gadolinium chloride has been reported elsewhere.[9] The crystals belong to the normal class of the monoclinic system,[10] although Benedicks[11] has classified them as tetragonal. The constants are $a:b:c = 1.4725:1:1.2185$; $\beta = 86° 20'$. The frequencies of the lines of seven of the most intense multiplets are given in Table I. Spectra from crystals prepared from both sources of gadolinium were photographed and the positions of the lines were found to be identical.

$GdBr_3 \cdot 6H_2O$.—The spectrum of this compound has also been described elsewhere.[12] The crystals are of the normal class of the monoclinic system. They have a notably

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(8) Freed [*Phys. Rev.*, 38, 2122 (1931)] photographed the spectra of Ce^{+++} compounds and found only broad, diffuse bands in the ultraviolet. He reasoned that as Ce^{+++} ion has only one 4f electron it must jump to the outside orbits in giving rise to these bands, and as they are diffuse all such jumps must be of this type. He attributed them to a 4f-5d jump. This, however, does not seem reasonable, for as Gibbs and White [*Phys. Rev.*, 33, 157 (1929)] have shown, if one plots the known gaseous energy levels of the isoelectric sequence Cs I, Ba II, La III and Ce IV, the curves are lines of small curvature which cross, and while the 6s orbit is lowest in Cs I, the 5d is probably so in Ce IV. From magnetic researches in solids it is known that for La III the 5d level is lowest, while for Ce IV (Ce^{+++}) it is the 4f. Between these two elements the curves must cross and unless they do so at a steep angle, which is not known to occur in any other case, the 4f-5d jump should be found in the far infra-red. The diffuse bands in the ultraviolet are probably due to electronic jumps to higher orbits which are slightly unstable.

(9) Freed and Spedding. *Phys. Rev.*, **34**, 945 (1929).

(10) Adolf Pabst, Am. *J. Sci.*, 22, 426 (1931).

(11) Benedicks, Z. *anorg.* Chem., 22, 403 (1900).

(12) Freed and Spedding, THIS JOURNAL, **52**, 3747 (1930)

different habit from the chloride crystals, but the axial ratios for the two are almost identical.[10] Because of its extreme deliquescence, only rough measurements were made.

$Gd_2(SO_4)_3 \cdot 8H_2O$.—On account of its small solubility, no large crystals were grown. Instead we have used conglomerates of small crystals fixed to quartz plates by means of a lacquer of pyroxylin dissolved in amyl acetate. The crystals are monoclinic, and although we have made no accurate measurements to confirm them, the data given in Groth, "Chemische Krystallographie" certainly cannot be far from correct. By a reorientation of $Gd_2(SO_4)_3\ 8H_2O$ crystals so that 101 becomes 001, 111 becomes 011 and 100 becomes 101, the new axial elements $83°26^1/_2'$ $a:b:c$ 1.4250:1:1.2224, may be obtained.

$$a:b:c = 3.0086:1:2.0068 \quad \beta = 118°2'$$

$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.—The salt was prepared by double decomposition between equivalent quantities of barium ethyl sulfate and gadolinium sulfate and was twice crystallized from solution in conductivity water. The crystals are hexagonal, showing the forms $(10\bar{1}0)$ (1120) $(10\bar{1}1)$ and (1121). They probably belong to the normal class. The ratio $c:a$ was found to be 0.5075, although Benedicks has stated that it is 0.5014.

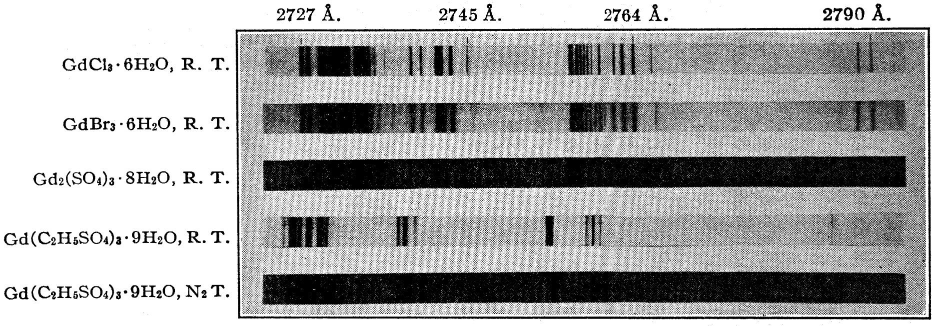

Fig. 1.

$Gd(BrO_3)_3 \cdot 9H_2O$.—A very dilute solution of $Gd_2(SO_4)_3 \cdot 8H_2O$ was added with vigorous stirring to an aqueous suspension of $Ba(BrO_3)_2 \cdot H_2O$. The mixture was kept on a steam-bath for several hours and then filtered. $Gd(BrO_3)_3 \cdot 9H_2O$ crystallized from the filtrate was obtained as large crystals on slow evaporation of a solution in conductivity water. The crystals belong to the hexagonal system, and probably to the normal class, although the possibility of pseudo-symmetry exists. Since the bromate ion begins to absorb near 3000 Å., only two multiplets were observed.

$Gd(NO_3)_3 \cdot 6H_2O$.—Gd_2O_3 prepared from the oxalate was dissolved in 3 N nitric acid and the excess acid removed by boiling. The salt was crystallized from a conductivity water solution. The crystals are triclinic with $a:b:c = 0.5571:1:0.7615$; $\alpha = 90°6'$, $\beta = 109°55'$; $\gamma = 109°48'$.

A Hilger E 185 spectrograph was used in all the work. The dispersion in the photographs of the bromate, bromide and chloride was about 3.0 Å. per mm. at 3000 Å. and 2.0 Å. per mm. at 2700 Å. The spectra of the sulfate and ethyl sulfate were photographed with an additional prism in the train and the dispersion was increased to 1.95 Å. per mm. at 3000 Å. and 1.35 Å. per mm. at 2700 Å.

Discussion of Results

In a previous letter[13] experimental evidence was presented which showed

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[13] Spedding, *Phys. Rev.*, **38**, 2080 (1931).

TABLE I

POSITIONS OF THE ABSORPTION LINES

$GdCl_3 \cdot 6H_2O$, R. T.[a]		$GdBr_3 \cdot 6H_2O$, R. T.	$Gd_2(SO_4)_3 \cdot 8H_2O$, R. T.	$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, R. T.		$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, N_2 T.		$Gd(BrO_3)_3 \cdot 9H_2O$, R. T.	$Gd(NO_3)_3 \cdot 6H_2O$, R. T.
Å.	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	Å.	cm.$^{-1}$	Å.	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
3117.04	32072.5	32061.5	.....	3110.07	32144.3	3110.96	32135.1	32132.2	32067.1
3114.87	32094.0	32095.1	.....	3108.55	32160.0	3109.21	32153.2	32145.7	32092.3
3112.14	32123.0	32123.3	.....	3107.78	32168.0	3108.26	32163.1	32152.6	32110.8
3109.86	32146.5	32146.5	.....					32157.3	32127.0
3060.54	32664.5	32656.8	.....	3053.87	32735.6	3054.64	32727.6	32708.7	
3057.08	32701.5	32698.6	.....			3051.83	32757.7	32749.1	
3053.61	32738.5	32738.7	.....	3051.32	32763.2	3051.66	32759.5	32761.0	
2792.67	35796.5	35792.3	35810.0	2786.12	35881.6	2786.81	35872.8		
2790.10	35830.5	35829.2	35840.7	2785.73	35887.7	2786.27	35879.7		
2788.70	35848.5	35850.5	35860.0	2784.40	35903.8	2784.99	35896.3		
2786.52	35876.5	35876.7	35884.0	2784.11	35907.6	2784.70	35899.9		
2765.90	36144.0	36137.1	36156.7	2759.73	36224.8	2760.40	36216.0		
2763.86	36170.5	36169.2D	36182.8	2758.85	36235.7	2759.46	36228.3		
2762.65	36186.5	36184.2D	36196.7	2758.30	36243.5	2758.89	36235.8		
2761.62	36200.0	36200.4D	36210.6	2758.07	36246.6	2758.68	36238.5		
2760.93	36209.0	36214.9	36228.7	2757.42	36255.1	2757.91	36248.6		
2759.86	36223.0	36221.1	36238.2						
2759.08	36234.5	36229.1	36244.5						
2758.53	36240.5	36236.8	36251.2			2754.81	36289.5		
				2754.11	36297.6T	2754.66	36291.4		
2758.11	36246.0	36243.3	36255.0						
						2754.49	36293.7		
2757.66	36252.0	36249.1	36259.0						
				2753.71	36304.0D	2754.26	36296.8D		
2757.20	36258.0	36255.4	36263.5						
			36271.5						
2756.59	36266.0D	36262.9D							

TABLE I (*Concluded*)

$GdCl_3 \cdot 6H_2O$, R. T.[a]		$GdBr_3 \cdot 6H_2O$, R. T.	$Gd_2(SO_4)_3 \cdot 8H_2O$, R. T.	$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, R. T.		$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, N_2 T.		$Gd(BrO_3)_3$-$9H_2O$, R. T.	$Gd(NO_3)_3$-$6H_2O$, R. T.
Å.	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	Å.	cm.$^{-1}$	Å.	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
2745.05	36418.5	36410.7	36431.5	2738.92	36499.9	2739.59	36491.0		
2743.09	36444.5	36441.4	36457	2737.95	36512.8	2738.42	36506.6		
		36455.7	36470.5						
2741.81	36461.5D			2737.63	36517.2	2738.28	36508.5		
		36463.5	36475						
						2737.70	36516.2		
2739.85	36487.5	36486.5	36497	2737.05	36524.9				
						2737.49	36519.0		
2738.69	36503.0	36502.1	36509	2736.35	36534.3	2736.84	36527.8		
2737.12	36524.0								
2735.80	36541.5	36528.8	.....						
2734.68	36556.5	36550.9	36552.5						
2734.12	36564.0D	36561.2	36568.5	2730.04	36618.4	2730.81	36608.4		
.....	.....	36570.3D	36580	2729.39	36627.4	2730.05	36618.6		
2732.70	36583.0	36580.7	36585			2729.5	36626.0D		
				2728.76	36635.8T				
2731.73	36595.0D	36593.1	36594.7			2729.09	36631.4		
		36603.5	36604	2727.73	36649.6	2728.36	36641.2		
2730.8	36608 T			2727.43	36653.7	2727.99	36646.3D		
		36609.0	36608.5	2726.62	36664.7	2727.18	36657.1		
2730.09	36618.0	36616.8	36618	2725.98	36673.2	2726.57	36665.3D		
			36624.3	2725.56	36678.9	2726.11	36671.5		
2729.27	36629.0	26623.8							
			36626			2725.50	36679.7		
				2724.84	36688.7D				
2728.64	36637.5	36631.6	36640.5			2725.26	36682.9		
2727.48	36653.0	36649.3	36658.9						
2726.85	36661.5	36659.8	36667.5						

[a] R. T. signifies room temperature; N_2 T., liquid nitrogen temperature. D indicates a double line; T, a triple line.

TABLE II

SEPARATIONS OF THE LINES IN THE MULTIPLETS[14]

	Hexagonal			Monoclinic					Triclinic
	$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$ Δν (cm.$^{-1}$)		$Gd(BrO_3)_3 \cdot 9H_2O$ Δν (cm.$^{-1}$)	$GdCl_3 \cdot 6H_2O$ Δν (cm.$^{-1}$)		$GdBr_3 \cdot 6H_2O$ Δν (cm.$^{-1}$)		$Gd_2(SO_4)_3 \cdot 8H_2O$ Δν (cm.$^{-1}$)	$Gd(NO_3)_3 \cdot 6H_2O$ Δν (cm.$^{-1}$)
Multiplet	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.
3110 Å.	15.7	18.1	13.5	21.5	26.5	33.6	36.0	Too faint	25.2
			6.9	29.0	29.0	28.2	29.5	to measure,	18.5
	8.0	9.9						but about	
			4.7	23.5	23.0	23.2	23.5	the same.	16.2
		30.1	40.4	37.0	40.0	41.8	43.0	See note	
3050 Å.	27.6							below	NO_3^-
		1.8	11.9	37.0	40.0	40.1	42.0		Absorption
	6.1	6.9	BrO_3^-	34.0	33.0	36.9	37.5	30.7	
2790 Å.	16.1	16.6	Absorption	18.0	20.0	21.3	22.5	19.3	
	3.8	3.6		28.0	29.0	26.2	27.5	24.0	
	10.9	12.3		26.5	28.0	32.1	26.0	26.1	
2765 Å.	7.8	7.5		16.0	17.5	15.0	19.0	13.9	
	3.1	3.7		13.5	16.0	16.2	14.5	13.9	
	8.5	10.1		9.0	15.5	14.5	17.0	18.1	
	12.9	15.6		26.0	27.0	30.7	34.5	35.5	
2740 Å.	14.4	1.9		17.0	20.0	14.3	15.0	13.5	
		7.7				7.8	6.0	4.5	
	7.7			26.0	24.5				
		2.8				23.0	25.0	22.0	
	9.4	8.8		15.5	16.6	15.6	15.0	12.0	

The multiplets at 2755 Å. and 2730 Å. are not included in this table since they are not completely resolved.

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[14] There may be two causes for the faintness of these lines. In the first place a conglomerate of many small crystals was photographed, and since these particular lines show strong selective reflection [Spedding and Bear, *Phys. Rev.*, **39**, 948 1932)], there is a tendency toward masking of the absorption. In the second place, at higher temperatures where the field fluctuations become large enough to cause a Paschen–Back effect, the excited levels become partially unstable and the lines blur and fade. At −190° all but one of the lines appear as do also the faint multiplets at 2990, 3180, 3250, 3500, 3920 and 3980 Å.

that all the lines arise from a single basic level, $^8S_{7/2}$, which is almost undisturbed by the crystal fields.[15] For this reason the positions of the lines and multiplets constitute effectivelyan energy level diagram of the excited levels. From Table I it is seen that the negative radicals have very little effect on the number and position of the multiplets which must therefore arise from electronic transitions of the Gd^{+++} ion. On the other hand, the number of lines and their positions within the multiplets are very much dependent on the nature of the chemical compound and evidently have their origin in the forces brought into play by the atoms surrounding the Gd^{+++}. The important factor in determining the splitting of the multiplet or excited level seems to be the crystal symmetry and not the negative radical, except in so far as the negative radical influences the crystal structure. The spectrum of the monoclinic $Gd_2(SO_4)_3 \cdot 8H_2O$ is almost identical with that of the monoclinic $GdCl_3 \cdot 6H_2O$, but very different from the hexagonal $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.

TABLE III

SHIFTS OF THE POSITIONS OF THE CENTERS OF THE MULTIPLETS FROM THOSE OF $GdCl_3 \cdot 6H_2O$ AT ROOM TEMPERATURE

	Hexagonal			Monoclinic				Triclinic
	$Gd(C_2H_5SO_4)_3.9H_2O$ $A\nu$ (cm.$^{-1}$)		$Gd(BrO_3)_3 \cdot 9H_2O$ $\Delta\nu$ (cm.$^{-1}$)	$GdBr_3 \cdot 6H_2O$ $\Delta\nu$ (cm $^{-1}$)		$Gd_2(SO_4)_3 \cdot$- $8H_2O$ $\Delta\nu$ (cm.$^{-1}$)	$GdCl_3 \cdot$- $6H_2O$ $\Delta\nu$(cm.$^{-1}$)	$Gd(NO_3)_3 \cdot$- $6H_2O$ $A\nu$ (cm.$^{-1}$)
Multiplet	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Liquid nitrogen temp.	Room temp.
3110 Å.	+48.4	+41.5	+38.0	– 2.4	– 7.9	....	– 1.4	– 9.7
3050 Å.	+52.5	+46.8	+38.1	– 3.5	– 8.8	....	– 2.0	...
2790 Å.	+57.2	+49.2	....	– 0.8	– 6.2	f10.7	– 3.5	...
2765 Å.	+59.1	$51.4	....	– 0.8	– 8.3	f13.1	– 5.4	...
2755 Å.	+53.5	+47.2	....	– 3.2	...	+11.5	– 4.1	...
2740 Å.	+56.2	$51.0	....	– 2.8	– 7.7	+10.5	– 2.3	...
2730 Å.	+56.8	+48.9	....	– 0.7	– 7.2	+10.7	– 9.9	...

The symmetry and separation of the ions in the lattice determine the magnitudes and directions of the fields on the electrons of the Gd^{+++} ion and thus the amount and type of splitting of the levels. The lines are so slightly affected by the mass of the negative ions that it is unreasonable to assign their origin to vibrational effects.

While we do not wish to generalize widely from so few examples we shall nevertheless call attention to some of the regularities we have observed in the data. The spectra of the monoclinic crystals are similar, with the lines appearing at nearly the same frequencies in the several cases. The shift in position of the lines between room temperature and that of liquid nitrogen is almost as great as the shift in position of lines from compound to compound.

(15) The basic ^8S level is only very slightly affected by the electric fields since its orbital moment is zero. As Kramers has pointed out, there should be small splitting due to second-order terms, and that this exists is clearly shown by the Zeeman patterns. In the accompanying pictures made at room temperature it can he observed only as a slight widening of the lines.

On the other hand, the spectra of the hexagonal crystals are distinctly different from those of the monoclinic, the multiplets being much narrower and shifted toward higher frequencies (Table III). The spacings are also different and in some cases fewer lines are observed.[16] Since only one band from a triclinic crystal has been measured, no conclusions can be drawn, but preliminary observations on gadolinium acetate, which is triclinic, indicate that its spectrum is different from that of both the hexagonal and monoclinic types.

These results are in qualitative agreement with predictions made by Bethe[6] on theoretical grounds. Quantitative results, however, are not to be expected as he made many simplifying assumptions which do not apply here.

Summary

Absorption spectra of gadolinium inn in crystals consist of lines which arise from electronic transitions from a single basic level $4f^7$, $^8S_{7/2}$, to excited levels which are non-degenerate through the influence of the electric fields of the neighboring ions. The amount and nature of the splitting depend upon the symmetry and separation of the ions in the lattice with higher symmetry corresponding to smaller separations of the levels.

We are continuing this work, extending the number of compounds in each crystal system and including anhydrous as well as hydrated compounds.

(16) While hexagonal crystallographic symmetry does not necessarily mean that there is hexagonal symmetry about the gadolinium ion, it is likely that the symmetry in the hexagonal crystals is much higher than that in the monoclinic.

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The Recording of Pressure and Time in Gas Explosions[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

Numerous investigations have been made of the increase in pressure during gas explosions in closed vessels. Generally, the instrument for indicating the pressure has been a thin metal diaphragm whose deflection is measured by a suitable optical arrangement. These diaphragms are, on the whole, very satisfactory for following rapid pressure changes. As they have been used, however, they possess at least two serious disadvantages. First, the tension of the diaphragm is dependent on the strength with which it is clamped into position. This clamping strength may be

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(3) Research Associate, University of Virginia.

altered during explosions and so vitiate the calibration of the diaphragm. Second, these diaphragms usually possess apparent hysteresis, which, we believe, is to be attributed not so much to the diaphragm itself as to the inelastic clamping gaskets commonly used.

We have developed a diaphragm indicator which effectively overcomes these difficulties and which has been used successfully for the recording of ozone explosions from which the specific heat of oxygen has been obtained.[4] This diaphragm and a method of dynamic calibration, together with several other features, will be described in this paper.

A sketch of the diaphragm clamped into the opening of the bomb is given in Fig, 1 and Fig. 1a.

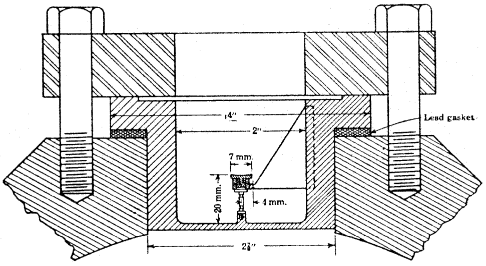

Fig. 1.

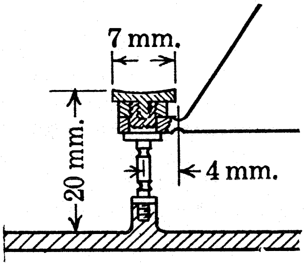

Fig. 1a.

A large cylinder of high-grade nickel steel is worked on the lathe to the shape given in the figure. The diaphragm itself forms the bottom of the piece and has a seat left in its center into which the piece carrying the mirror can be screwed rigidly by means of a conical thread. This piece consists of a thin rod of spring steel in which two necks have been cut to allow flexibility. Over the end of the central piece is fitted a thin ring which is kept rigid by means of a small nut. The ring is a part of a heavy piece of the same spring steel which is firmly dovetailed into the heavy wall of the diaphragm piece Immediately adjacent to the ring and part of the same piece, another flexible neck is cut The mirror, which is screwed into the top of the central piece by means of a conical thread, is concave and made of high-grade stainless steel. It was ground very accurately to a focal length of 1.5 meters by the astronomical instrument makers, John A. Brashear Co., Pittsburgh. Assembled, the whole mechanism was rigid as though made of one piece. When pressure is exerted on the back face of the diaphragm the center piece tends to move out and is forced to deflect to the right by reason of the necks. The mirror therefore moves about a circle with a radius of 4 mm., the distance between the center of the central rod and the center of the adjacent neck. The magnification of this system for a distance of 1 5 meters between the mirror and the film is about 1000. Thus only very small deflections of the diaphragm itself need take place for reasonable movements of the light point on the film This has an obvious and important advantage, since the diaphragm can be made relatively thick and so possess a high natural frequency which is desirable in explosion experiments.

The whole piece was clamped rigidly into the opening of the bomb by bolts and a flange as shown in the figure. The strain was applied to the rim of the piece, leaving the diaphragm proper perfectly free. It was impossible for it to change its position as a result of explosions.

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(4) Lewis and von Elbe, THIS JOURNAL, 55, 511 (1933).

Calibration of Diaphragm.—Calibrations were made in two ways, dynamically and statically. In the dynamic method the pressure was applied to the diaphragm in a time interval of about 0.01 second, which was about the same order as the time during which the pressures were released in explosions under investigation. The results showed that with this type of diaphragm there was no difference between the two methods of calibration. This strongly indicates that hysteresis effects are negligible for the deflections employed.

For the dynamic calibration, the device shown in Fig. 2 was used. It was fitted into the bomb through a hole directly opposite the hole carrying the diaphragm. The distance between the end face of the calibration cylinder and the face of the diaphragm was about $^1/_{16}$ inch. It is essential for correct results that no part of the diaphragm piece be touched by the calibration cylinder. The space between was sealed from the rest of the bomb space by means of a rubber gasket. The cylinder was filled with hydrogen gas at a known pressure, which was suddenly released onto the diaphragm by quickly turning a quadruple screw which opened a needle valve. A large accurately calibrated gage of the Bourdon type was in the system all the time. The time during which the total pressure was released on the diaphragm depended on the gas used and not on the above manipulations. This was made clear by calibrations with carbon dioxide gas, which showed conclusively that the time required to reach the final pressure in the calibration was a function of the viscosity of the gas used. The line on the film representing the pressure increase coincided with the final pressure line on the film for both carbon dioxide and hydrogen in a time of the order of 0.01 second from the commencement of pressure increase

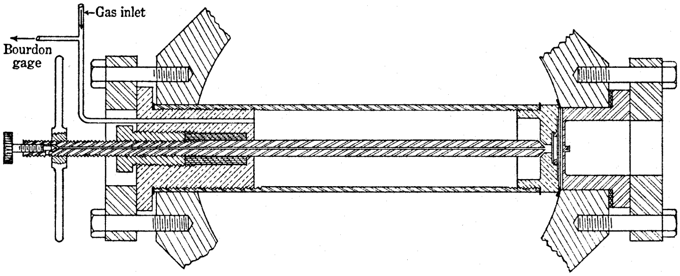

Fig. 2.

The calibration cylinder is easily removed and replaced whenever it is desired to make a new calibration. It may be stated, however, that the diaphragm described above showed the same calibration after it was removed from the bomb and replaced again on several occasions.

Recording on the Film of Instant of Passage of Explosion Spark.—Since it was desired to make time–pressure analyses of the explosions taking place in the bomb,[5] a device was used which essentially is not new but which deserves description. An auxiliary spark was placed at the focus of a parabolic mirror which was built into the housing covering the rotating film. This spark was in series with the main spark at the center of the bomb. By means of a slit the auxiliary spark made a sharp narrow line on the film at right angles to its movement. Both sparks passed when contact was broken by a switch operating with the moving shaft. The procedure was to hold the film stationary and to record the fine light point from a carbon arc and the line from the auxiliary spark on the film. (The bomb spark was disconnected during this operation.) The film was now allowed to rotate at a constant speed and both sparks allowed to pass. The original distance between the auxiliary spark line and the light point made when

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(5) Lewis and von Elbe, in preparation.

the film was stationary, measured back from the new auxiliary spark line made with film in motion, located the point on the film at which the light point was when the spark passed in the bomb.

Summary

A diaphragm indicator for measuring the pressures developed in explosions is described. Its essential advantages are sensitivity, freedom from hysteresis for the deflections employed, and constancy. A method of calibrating dynamically, without removing the diaphragm from the explosion chamber, is described in which pressures are released against the diaphragm in a time interval of the same order as in explosians. It is shown that for this type of diaphragm the observed deflections for a given range of pressures investigated are the same for dynamic as for static calibration.

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Thermal Equilibrium between Oxygen Molecules and Atoms[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

During the course of experiments carried out at the Pittsburgh Experiment Station of the U. S. Bureau of Mines on the direct determination of the specific heat of oxygen at high temperatures by exploding mixtures of ozone and oxygen,[4] it was necessary to know the degree of dissociation in order to obtain accurate values of the specific heats. Since this information is not available in the literature, we have set up an equation for the equilibrium constant of the reaction 2O O_2 expressed as

$$K_p = \frac{[p_{\text{at.}}]^2}{p_{\text{mol.}}} \tag{1}$$

One commences with the well-known fundamental thermodynamic equation

$$AF = AH - TAS \tag{2}$$

For the condition of equilibrium between atoms and molecules of oxygen $AF = 0$, and therefore

$$0 = (\Delta H/T) - AS \tag{3}$$

The entropy per mole of each participant in the reaction is given by

$$S = C_{p_0} \ln T + \int_0^T \frac{C_{\text{vib}}}{T} \mathrm{d}T - R \ln p + Ri + C_{p_0} \tag{4}$$

where C_{p_0} is the constant part of the specific heat at the temperature T,

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(4) Lewis and von Elbe, THIS JOURNAL, 55, 511 (1933).

i. e., due to translation and rotation; $C_{\text{vib.}}$ is the specific heat due to vibrations of the molecule, p is the partial pressure of each constituent at equilibrium, i is the chemical constant of each constituent.

Equation 4 includes the Sackur equation for translational entropy and also the rotational entropy for the case that rotation is fully excited. This may be shown by comparison with the statistical formulas

$$S_{\text{trans.}} = {}^5/_2 R \ln T - R \ln p + {}^3/_2 R \ln m + R \ln \left[(2\pi)^{3/2} k^{5/2}/h^3\right] + R \ln g + {}^5/_2 R \qquad (3a)$$

$$S_{\text{rot.}} = {}^2/_2 R \ln T - R \ln (\text{symmetry number}) - R \ln \frac{h^2}{8\pi^3 Ik} + {}^2/_2 R \qquad (3b)$$

Adding 3a and 3b results in equation 3, less the vibrational part, *viz.*

$$S_{\text{trans.}+\text{rot.}} = {}^7/_2 R \ln T - R \ln p + Ri + {}^7/_2 R \qquad (3c)$$

Giauque and Johnston[5] have calculated the entropy of molecular oxygen from 0°K. to 298°K. which includes ($S_{\text{trans.}} + {}_{\text{rot.}} + {}_{\text{vib.}} + i_{\text{mol.}}$) where $i_{\text{mol.}}$ is the chemical constant of the oxygen molecule. Their value for this at one atmosphere pressure is 49.03 entropy units which we shall employ. Equation 3 transforms to

$$0 = \frac{\Delta H}{T} - \left[2S_{\text{at.}} - \left(S_{\text{mol.}}\Big|_{298}^{T} + 49.03\right)\right] \qquad (5)$$

where $S_{\text{at.}}$ represents the entropy of the oxygen atom and $S_{\text{mol.}}\Big|_{298}^{T}$ is the part of the entropy of the oxygen molecule between 298°K. and T°K. This expands to

$$0 = \frac{\Delta H_0}{T} + \frac{\int_0^T 2C_{p_{\text{at.}}}}{T}\,\mathrm{d}T - \frac{\int_0^T C_{p_{\text{mol.}}}}{T}\,\mathrm{d}T - 2S_{\text{at.}} + S_{\text{mol}}\Big|_{298}^{T} + 49.03 \qquad (6)$$

Substituting for the entropy, equation 4, one obtains

$$0 = \frac{\Delta H_0}{T} + \frac{\int_0^T 2C_{p_{\text{at.}}}}{T}\,\mathrm{d}T - \frac{\int_0^T C_{p_{\text{mol.}}}}{T}\,\mathrm{d}T - 2R\left[{}^5/_2 \ln T - \ln p_{\text{at.}} + i_{\text{at.}} + {}^5/_2\right] +$$
$$R\left[{}^7/_2 \ln T + \frac{1}{R}\int_0^T \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T - \ln p_{\text{mol.}} + {}^7/_2 + i_{\text{mol.}} - \left({}^7/_2 \ln 298 + \right.\right.$$
$$\left.\left.\frac{1}{R}\int_0^{298} \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T - \ln 1 + {}^7/_2 + i_{\text{mol.}}\right)\right] + 49.03 \qquad (7)$$

The expression $\int_0^{298} (C_{\text{vib.}}/T)\,\mathrm{d}T$ is negligibly small. Transposing, dividing by R and changing to logs to the base 10

$$\log \frac{[p_{\text{at.}}]^2}{p_{\text{mol.}}} = -\frac{\Delta H_0}{2.3\,RT} + \frac{3.5}{2.3} + 5 \log \mathrm{T} + \frac{2i_{\text{at.}}}{2.3} - 3.5 \log T + 3.5 \log 298 -$$
$$\frac{49.03}{2.3\,R} - \frac{1}{2.3\,R}\int_0^T \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T \qquad (8)$$

ΔH_0 is the heat of dissociation at absolute zero which is equal to 117,300 calories per mole.[6] This value is for dissociation from the $^3\Sigma$ state of the

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(5) Giauque and Johnston, Tars JOURNAL, **51**, 2300 (1929).

(6) Paschen, *Naturwissenschaften*, **84**, 752 (1930); Sommer, *ibid.*, **34**, 752 (1930); Frerichs, *Phys. Rev.*. **36**, 398 (1930).

oxygen molecule to the ${}^3P_2$ state of the atom (see below). The expression $\int_0^T (C_{\text{vib.}}/T)\,dT$ can be evaluated by Einstein functions $(F - F_0)/T$.[7] There is practically no difference between the values so derived and the values derived from the spectroscopic vibrational–rotational levels of the molecule. This is known by a comparison of such calculations.[4] This also makes it unnecessary to account for the change of the moment of inertia $\mathbf{I}$ in $i_{\text{mol.}}$ for higher rotational levels (compare equation 3b). Using the value of **1556.4** cm.$^{-1}$ for the separation of the first vibrational level of the oxygen molecule[8] we obtain

$$\frac{\beta\nu}{T} = \frac{2229}{T}$$

from which $(F - F_0)/T$ can be evaluated. $i_{\text{at.}}/2.3$ is expressed by the well-known equation[9]

$$\frac{i_{\text{at.}}}{2.3} = -1.587 + 1.5 \log M + \log g \qquad (9)$$

where M is the atomic weight of the oxygen atom and g is the statistical weight of the atomic state.

The value of g is derived in the following way. The ground level of the oxygen atom is a triplet state in which the three terms ${}^3P_2$, ${}^3P_1$ and ${}^3P_0$ are separated by small energy differences: ${}^3P_2 - {}^3P_1 = 447$ calories, ${}^3P_2 - {}^3P_0 = 635$ calories. The multiplicity of the separate terms can be obtained from measurements of magnetic susceptibility made by Kurt and Phipps.[10] They find a multiplicity of 5 for the ${}^3P_2$ term, 3 for ${}^3P_1$ and 1 for ${}^3P_0$.

The statistical weight g of the atomic state is given by the sum of the products of the multiplicity of the terms ${}^3P_2$, ${}^3P_1$ and ${}^3P_0$ and the probability of the atoms being in each of these states, referred to the lowest state ${}^3P_2$. Then

$$g = 5 + 3e^{-447/RT} + e^{-635/RT} \qquad (10)$$

The complete equation for $\log K_p$ is

$$\log K_p = -\frac{117300}{4.571\,T} + 1.5 \log T - \frac{(^1/_3 F/T;\ \beta\nu/T = 2229/T)}{4.571} - 0.104 + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) \qquad (11)$$

However, equation 11 must be revised by the addition of another term relating to the oxygen molecule, for the following reasons.

In our experimental determination of the specific heat of oxygen up to 2500°K., the results show that the experimental values of the specific heats are always higher than those calculated from the vibrational–rotational levels of the normal state of the molecule[4] in the temperature range investi-

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(7) Landolt and Bornstein, Supplementary Vol. 1, p. 702.

(8) Mecke and Baumann, Z. Physik, 78,139 (1931); Babcock and Hoge, *Phys. Rev*, 39, 650 (1932)

(9) See, for example, A. Eucken, "Lehrbuch der chemischen Physik," Leipzig, 1930, pp. 246–247, or the constant part of equation 3a above.

(10) Kurt and Phipps. Phys. Reu., 84, 1357 (1929).

gated. The difference becomes more pronounced with increasing temperature. It has been pointed out[11] that this difference can be accounted for by the predicted metastable 'A level of the neutral oxygen molecule. It turns out that the separation of this level from the ground state $^3\Sigma$ is 0.75 ± 0.05 volt or 17,200 ± 1000 calories.

The ratio of the multiplicities of the $^1\Delta$ and $^3\Sigma$ states is $^1\Delta/^3\Sigma = {}^2/_3$.[11] We therefore obtain for the statistical weights an expression for the molecule similar to that found for the atom: namely

$$\log g_{\text{mol.}} = \log (3 + 2e^{-17{,}200/RT}) \tag{12}$$

This term, except that part representing the multiplicity of the $^3\Sigma$ state, namely, log 3, which is already included in Giauque and Johnston's value of the entropy of the oxygen molecule, must be subtracted from equation 11.

The revised equation for log K_p is then

$$\log K_p = -\frac{117{,}300}{4.571\,T} + 1.5 \log T - \frac{\left(\frac{1}{3}\frac{F}{T}, \frac{\beta\nu}{T} = \frac{2229}{T}\right)}{4.571} - 0.104 + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) - \log \left(1 + \frac{2}{3} e^{-17{,}200/RT}\right) \tag{13}$$

We believe that this equation is valid up to 4000°K. and may apply up to 5000°K. without serious error. The following table contains the calculated values of log K_p, and the per cent. dissociation x for one atmosphere pressure up to 5000°K. The value of x is derived from the expression

$$K_p = \frac{4x^2}{1 - x^2} P \tag{14}$$

TABLE I

VALUES OF LOG K_p AND DEGREE OF DISSOCIATION OF OXYGEN AT ONE ATMOSPHERE PRESSURE

T, °K.	Log K_p	x, %	T, °K.	Log K_p	x, %
1400	−11.968	5×10^{-5}	2800	−2.495	2.83
1600	− 9.610	8×10^{-4}	3000	−1.858	5.88
1800	− 7.772	6.5×10^{-3}	3500	−0.577	24.9
2000	− 6.298	0.0353	4000	+0.379	61.3
2200	− 5.091	0.142	4500	+1.120	87.6
2400	− 4.078	0.452	5000	+2.715	96.4
2600	− 3.228	1.22			

Experimental proof for the correctness of the degree of dissociation is given by experiments on the specific heat of oxygen.[4] At high temperatures, say 2400°K., the experimental points are far above the values of specific heats calculated from the vibrational–rotational levels of the molecule. This is accounted for by dissociation and the $^1\Delta$ level contribution to the specific heat. While at lower temperatures the dissociation rapidly disappears, the $^1\Delta$ level contribution decreases slowly. Therefore, at lower temperatures the difference between experimental values and those

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(11) Lewis and von Elbe, *Phys. Rev.*, 41,078 (1932).

from the vibrational–rotational levels is due only to the $^1\Delta$ level contribution. One can determine the separation of the $^1\Delta$ level from the $^3\Sigma$ level, from the experimental points at lower temperatures, *i. e.*, about 2000°K., and plot the new specific heat values given by the $^1\Delta$ level curve up to 2400°K. From the difference between this curve and the weighted mean of a large number of experimental points at this temperature, one obtains the degree of dissociation given by the above formula.

Summary

A rigorous equation is derived for the equilibrium constant of the reaction $2O \rightleftharpoons O_2$ with the aid of optical data and new determinations of the specific heat of oxygen at high temperatures. A table is given for log K_p and the degree of dissociation up to 5000°K. Experimental proof for the correctness of the degree of dissociation is given.

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The Specific Heat of Oxygen at High Temperatures from Ozone Explosions and the Energy of the $^1\Delta$ Level of the Neutral Oxygen Molecule[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

The theory of specific heats of gases demands that at high temperatures they be represented by the classical translational and rotational values of the specific heats plus the vibrational contribution. As far as molecular vibrations can be considered to be harmonic they are represented simply by the Planck–Einstein equation for an harmonic oscillator. This equation expressing the mean vibrational specific heat of one mole of gas for one vibrational degree of freedom between 300°K. and T is given by

$$\bar{C}_{\text{vib}300}^{\,T} = \frac{1}{T - 300}\left(\frac{\epsilon_0}{e^{\epsilon_0/RT} - 1}\right) \qquad (1)$$

where ϵ_0 is the energy in calories per mole of the first vibrational level of the degree of freedom of the molecule considered. Tables for this function are available for example in Landolt–Börnstein.[4]

For a more rigid calculation involving the anharmonic oscillations of the actual molecule, one would use the actual separations of the higher vibrational levels wherever these are available from spectroscopic data, using the same statistical principles underlying the Planck–Einstein formula.

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(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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(4) Landolt-Börnstein, Supplementary Volume 1, p. 702.

The equation would then read

$$\bar{C}^{\,T}_{\mathrm{vib}_{300}} = \frac{1}{T-300}\,\frac{\epsilon_1 e^{-\epsilon_1/RT} + \epsilon_2 e^{-\epsilon_2/RT} + \epsilon_3 e^{-\epsilon_3/RT} + \ldots\ \epsilon_n e^{-\epsilon_n/RT}}{1 + e^{-\epsilon_1/RT} + e^{-\epsilon_2/RT} + e^{-\epsilon_3/RT} + \ldots\ e^{-\epsilon_n/RT}} \qquad (2)$$

where ϵ_1 is the separation of the first vibrational level above the ground state of the molecule, ϵ_2 is the separation of the second vibrational level above the ground state of the molecule, etc., expressed in calories per mole.

To obtain the total mean specific heat there must be added to the vibrational contribution given by equation 2, $^5/_2R$ (translational and rotational contributions) and a small amount due to the fact that the rotational levels are not equally spaced but become more closely packed with each successively higher vibrational level (see below). This closer packing of the rotational levels favors the excitation of the molecule above that which would exist were the packing of the rotational levels identical. In addition, if there is an electronic level lying close enough to the ground state of the molecule so that an appreciable number of molecules reach this level at a temperature T, a further contribution to the specific heat will be made from this source.

The results of the present investigation of the specific heat of oxygen indicate that the predicted but hitherto unknown $^1\Delta$ electronic level of the oxygen molecule[5] must be considered. It is possible from our data to locate this level at 0.75 ± 0.05 volt or 17,200 ± 1000 calories above the normal $^3\Sigma$ state of the molecule.[6]

It is extremely fortunate in an experimental determination of the specific heat of oxygen to be able to explode a single gas such as ozone which results only in one product, namely, the gas being studied. The decomposition of ozone seems to be the only such reaction provided by nature. In addition, it should perhaps be the simplest and most direct case to lend itself to a fundamental study of the propagation of explosions in space. The latter study is in progress in this Laboratory at the Pittsburgh Experiment Station, the details of which will appear in a later publication.

Apparatus, Materials **and** Experimental Procedure.—The bomb in which the explosions were carried out was a chrome-plated iron sphere of 300 mm. diameter. The pressure recording diaphragm used and the method of calibration are described in the preceding publication[7] A 10-inch Duragauge of the Bourdon type reading accurately to 0.1% used in this work, was calibrated by the Bureau of Standards. After the completion of the experiments it was recalibrated by us with a dead weight tester calibrated by the Bureau of Standards and found to check the original calibration. Ignition of the mixture was accomplished by a small spark between two platinum points placed accurately in the center of the sphere. The wires were fused into a glass capillary tube $^3/_{32}$ inch outer diameter which entered the sphere through a hole in the end plug. No organic material was used in construction. With the bomb chrome-plated, the interior became perfectly passive to the presence of ozone after it had been exposed to the gas

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(5) Mulliken, *Phys. Rev.*, 82, 213, 887 (1928); Hund, *Z. Physik*, 51, 759 (1928). 63, 726 (1930); Hückel, *ibid.*, 60, 442 (1930).

(6) Lewis and von Elbe, *Phys. Rev.*, 41, 678 (1932).

(7) Lewis and von Elbe, THIS JOURNAL, 65, 504 (1933).

for some time. This was desirable, since it allowed one to fill the bomb with any desired mixture of ozone and oxygen.

The ozone was prepared in the liquid state with a purity of nearly 100% (any impurity being oxygen) by the method of Riesenfeld and Schwab,[8] the usual precautions[9] being taken to exclude organic matter. It was allowed to evaporate very slowly[10] into the bomb by surrounding the tube containing the liquid ozone with an empty unsilvered Dewar flask which just previously had been flushed with liquid air.

Pressure readings were taken with a mercury manometer protected by a buffer of oxygen gas. An accurate manometer was constructed with a vernier attachment and readings were made on accurate steel scales. The valves through which the gases entered the bomb were stainless-steel needle valves The temperature of the gases in the bomb was taken with a mercury thermometer inserted deeply into the wall of the bomb and maintained in mercury for good thermal contact. The temperature was read when thermal equilibrium had been established.

After the ozone had entered the bomb its pressure was measured and a suitable amount of pure oxygen was added (electrolytic oxygen with the hydrogen burned out and dried) and allowed to stand to ensure mixing. Measurements of the pressure were taken between time intervals just previous to explosion to measure decomposition, if any. After the bomb had been in use a little while, no decomposition was observed. The explosion was carried out and a time–pressure record was obtained[11] on a rotating photographic film. After the explosion, the temperature in the bomb was allowed to come to equilibrium, and the temperature and pressure readings were taken. The pressure before and after the explosion, corrected to a suitable common temperature. allowed one to determine accurately the amount of ozone originally present.[12]

Method of Calculation.—A series of explosions was made with mixtures having ratios of oxygen to ozone of 0.85 to 3.5, resulting in explosion temperatures ranging between 1400 and 2500°K. Initial pressures were varied between 300 and 760 mm., while the final explosion pressures ranged from about 3000 to 5000 mm.

The method of evaluating the mean specific heat is as follows. The experimental data consist of P_i, initial pressure before explosion; T_i, initial temperature of gases before explosion; P_{ie}, the pressure after the explosion measured at T_i; ΔP, increase in pressure from P_i to maximum explosion pressure as measured on film. All pressure readings were reduced to a mercury column at 0°, accounting for the temperature coefficient of the metal scale. All gas pressures P_{ie} were reduced to the common temperature, T_i.

The reaction considered is $2O_3 = 3O_2 +$ heat of decomposition. For the case of no dissociation

$$T_e = \frac{P_e \times T_i}{P_{ie}} \tag{3}$$

where P_e is the total explosion pressure consisting of $\Delta P + P_i$, and T_e is

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(8) Riesenfeld and Schwab, *Ber.*, 66, 2088 (1922).

(9) See, for example, Lewis and Feitknecht. THIS JOURNAL, 63,2910 (1931).

(10) The amount of liquid ozone required for one experiment varied from 4 to 10 cc. Care should be exercised in handling these quantities of liquid ozone. If allowed to evaporate too fast or violently, powerful explosions result.

(11) For details of this time–pressure re-ording device see Ref. 7

(12) Ozone decomposition was always complete.

the final explosion temperature. The number of moles of oxygen per mole of ozone present before the explosion is given by

$$\frac{P_i - 2(P_{ie} - P_i)}{2(P_{ie} - P_i]} = \frac{n_{O_2}}{\text{nor}} \tag{4}$$

The heat of decomposition at constant volume of 1 mole of ozone is 34,220 ± 280 calories.[13] Then

$$\bar{C}_{v_{T_i}}^{Te} = \frac{34220}{\Delta T[1.5 + (n_{O_2}/n_{O_3})]} \tag{5}$$

where $\bar{C}_{v_{T_i}}^{Te}$ is the mean specific heat at constant volume between T_i and T_e. T_i was always about 300°K.

For the case of dissociation equation **3** changes to

$$T_e = \frac{P_e}{(1+x)}\frac{T_i}{P_{ie}} \tag{3a}$$

The value calculated from equation (5) is too high by an amount C_D, the specific heat contribution calculated from the degree of dissociation into atoms. This is given by

$$\bar{C}_D = \frac{H_{v_T}\, x}{\Delta T} \tag{6}$$

where H_{v_T} is the heat of dissociation of the oxygen molecule at constant volume and temperature T. It is calculated from the expression

$$H_{v_T} = H_0 + \int_0^T (2C_{v_{at.}} - C_{v_{mol.}})\mathrm{d}T \tag{7}$$

where H_0 is the heat of dissociation at O°K. and is equal to 117,300 calories.[14] $C_{v_{at}}$ is the specific heat of the oxygen atom which is equal to $3/2R$, and $C_{v_{mol.}}$ is the specific heat of the oxygen molecule, which is equal to $^5/_2R$ plus the vibrational specific heat contribution up to T°K. x is the degree of dissociation given by the formula

$$K_p = \frac{[p_{at.}]^2}{p_{mol.}} = \frac{4x^2}{1 - x^2} P_e \tag{8}$$

The equation for log K_p is[15]

$$\log K_p = \frac{-117{,}300}{4.571T} + 1.5 \log T - \frac{(1/3F/T;\ \beta_\nu = 2229)}{4.571} - 0.104 + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) - \log (1 + {}^2/_3e^{-17200/RT}) \tag{9}$$

Below 1800°K., dissociation is negligible.

Results

The results of the experiments are given in Fig. 1. The points represent the mean specific heats between 300 and T°K. at constant volume corrected for dissociation.

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[13] Günther, Wassmuth and Schryver, *Z. physik. Chem.*, *168*, 297 (1932); see also Kailan and St. Jahn, *Z. anorg. Chem.*, 68, 243 (1910).

[14] Paschen, *Naturwissenschaften*, 34, 762 (1930); Sommer, *ibid*, 34, 752 (1930); Frerichs, *Phys. Rev.*, 36, 398 (1930).

[15] Von Elbe and Lewis, THIS JOURNAL, **55**, 507 (1933).

These will now be compared with the theoretical values of the specific heats. The dotted line represents the specific heats according to the Planck–Einstein equation. A value of 1556.4 cm.$^{-1}$ for the separation of the first vibrational level of the oxygen molecule[16] or 4425.6 calories was used for ϵ_0, giving a value of $\beta\nu = 2229$.

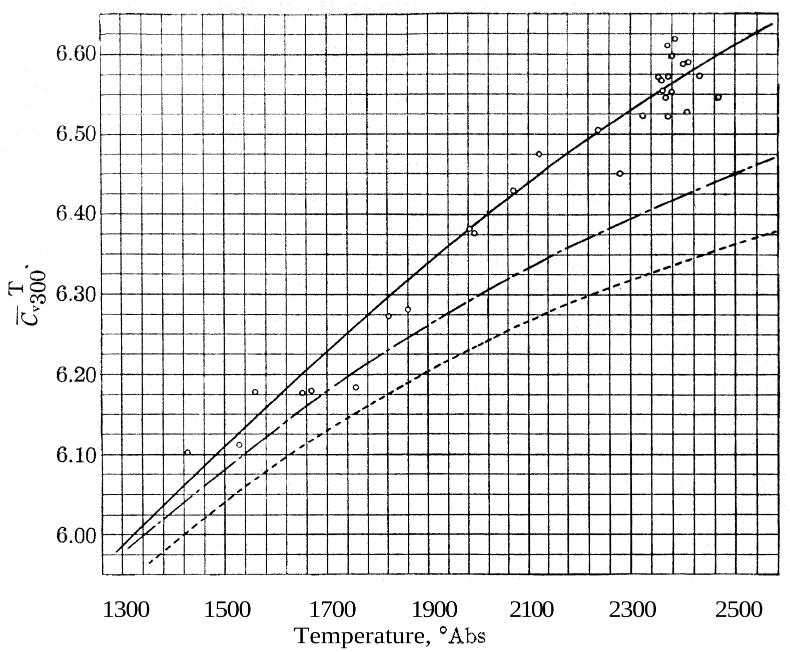

Fig. 1.—Specific heat of oxygen from ozone explosions: - - - - - theoretical specific heat of oxygen from Planck–Einstein equation; — - — theoretical specific heat from values of vibrational–rotational levels of oxygen molecule; ———— new specific heat curve which includes $^1\Delta$, level contribution; ○ experimental values corrected for dissociation.

The more exact theoretical curve is given by the dot-dashed line as calculated from the known separations of the higher vibrational levels of the oxygen molecule, using equation *2*. Professor R. T. Birge kindly provided us with new extrapolated values of the separations of the lower nine levels, which were used. The extrapolated separation of the first level is 1553.8 cm.$^{-1}$, whereas the observed value is 1556.4 cm.$^{-1}$. We solved this difficulty by using the differences between the extrapolated separations and applying them to an initial separation equal to the observed, 1556.4 cm.$^{-1}$. The separations used are as follows

Vibrational level, v =	1/2	3/2	5/2	7/2	9/2	11/2	13/2	15/2	17/2
ΔG, cm.$^{-1}$	1556.4	1533.9	1511.4	1488.9	1466.3	1443.7	1421.1	1398.5	1375.9

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(16) Mecke and Baumann, *Z. Physik*, 73, 139 (1931); Babcock and Hoge, *Phys. Rev.*, 39, 560 (1932).

Our values of the mean vibrational specific heats so calculated, check with the values calculated by Dr. H. L. Johnston[17] except for the small amount which is due to the fact that the rotational levels crowd together more closely with increasing vibrational states. We call this latter contribution "rotational stretching" of the molecule. For the value of this rotational stretching we are indebted to Dr. Johnston.

Discussion of Results

The experimental values are always higher than the theoretical curve in the temperature range investigated, the difference becoming more pronounced with increasing temperature.

Analysis of the slope of the cooling curves in these explosions led us to believe that heat losses before maximum pressure is established are negligible. Heat losses if any could only be confined to radiation losses because the burned gas is isolated from the wall until the end of the combustion by unburned gas, the increase in temperature of which due to adiabatic compression is small.[18] But even the radiation losses at thermal equilibrium are entirely negligible as is shown by the small slope of the cooling curves on the film. The cooling, as represented by these curves, is by far due to cooling by conduction. Any appreciable activated radiation, that is, radiation due to transitions from higher electron levels, is out of the question, because the first radiating electron levels above the normal state are too high for appreciable numbers of molecules and atoms to be raised to them at the temperature of these explosions. Transition from the predicted $^1\Delta$ metastable level is not possible.

It is inconceivable that so-called "afterburning" should exist in the present case, since the ozone molecule is so sensitive to decomposition and the collision frequency in the flame front is already so high. Moreover, afterburning would round off the maximum in the pressure diagram of which there is no indication especially in the fastest explosions.

The difference between the experimental and theoretical curves must therefore be due to the presence of the predicted $^1\Delta$ metastable level.

It may be remarked that there is a certain amount of scattering in the experimental results, the maximum deviation from the mean being about 0.8%.

By running a considerable number of explosions around 2400°K. we were able to locate an experimental point at 2385°K. which had a weighted mean of $\bar{C}_v = 6.56 \pm 0.02$. The difference of $\bar{C}_v$ at 2385°K. between the theoretical and experimental points is 0.146 ± 0.02.

If n_{1_Δ} is the fraction of one mole of oxygen raised to the $^1\Delta$ level whose energy is E_{1_Δ} calories per mole, then

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(17) Private communication.

(18) A detailed analysis of the movement of the flame front in these explosions in the spherical bomb will be given in a forthcoming article.

$$0.146 = \frac{n_{1_\Delta}}{T - 300} E_{1_\Delta} \tag{10}$$

The fraction n_{1_Δ} is given by the statistical relation[6]

$$n_{1_\Delta} = \frac{N_{1_\Delta}}{N_{3_\Sigma} + N_{1_\Delta}} \sim {}^2/_3 e^{-E_{1_\Delta}/RT} \tag{11}$$

E_{1_Δ} is equal to 17,200 ± 1000 calories or 0.75 ± 0.05 volt.

The solid lines is the new mean specific heat curve which now includes the ${}^1\Delta$ Level contribution, It is seen that it fits the experimental points very well along the whole range.

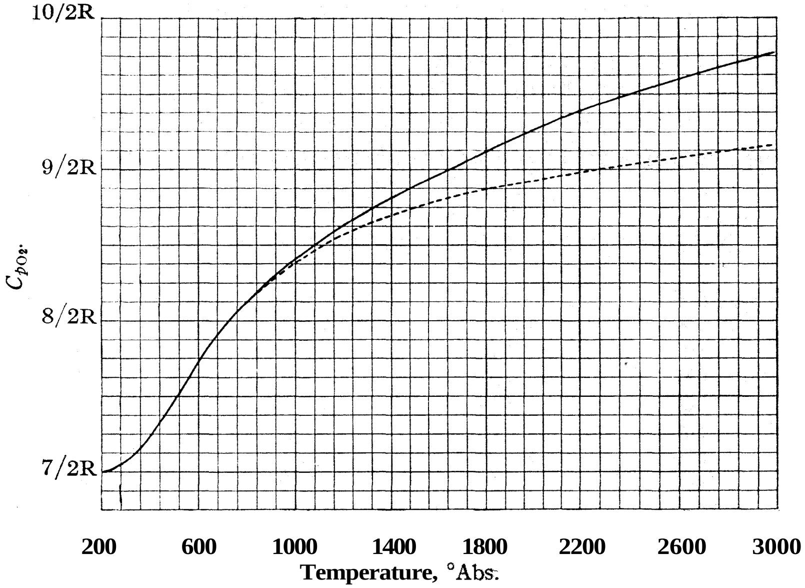

Fig. 2.—C_p of oxygen molecule against absolute temperature: - - - - - includes translation + rotation + vibration + stretching + R + ${}^1\Sigma$ level contribution; ———— same + ^{1}A level contribution.

The results also give a fair experimental proof of the equation for the dissociation of oxygen molecules into atoms proposed by us, for if the degree of dissociation were substantially different from the values calculated at about 2400°K., one would not be able to separate the part of the specific heat due to the ${}^1\Delta$ level and have the curve of the latter fit the experimental points at lower temperatures.[14]

The total specific heat of oxygen up to temperatures of 3000°K. is composed of the translational, rotational, vibrational, rotational stretching and electronic contributions. To calculate the true specific heats from the mean specific heats is a laborious operation. To enable one readily to evaluate the true specific heat of oxygen per mole at any temperature between 200 and 3000°K., we have carried out these operations and have developed two empirical formulas for two ranges of temperature.

The curve for C_p is plotted in Fig. 2. The dotted curve includes translation, rotation, vibration, stretching and the contribution from the $^1\Sigma$ level, which is 37,300 calories above the ground state. The latter contribution to the specific heat becomes appreciable at about 2700°K. The addition of the $^1\Delta$ level contribution to the dotted curve gives the true specific heat and is given by the solid curve.

The formulas representing this curve are

1. Valid between 200 and 800°K.

$$C_{p_{O_2}} = 6.951 + 0.068 \times 10^{-4} (T - 200)^2 - 0.0048 \times 10^{-6} (T - 200)^3 - 0.000225 \times 10^{-8} (T - 200)^4$$

2. Valid between 900 and 3000°K.

$$C_{p_{O_2}} = 6.951 + 2.400 \times 10^{-3} (T - 300) - 0.700 \times 10^{-6} (T - 300)^2 + 0.0270 \times 10^{-12} (T - 300)^4$$

Table I contains values of C_p from 200 to 3000°K.

TABLE I

VALUES OF TRUE SPECIFIC HEAT OF OXYGEN FROM 200 TO 3000°K.

T, °K.	True C_p	C_p from empirical formulas	Deviation of formula, %
200	6.951	6.951	0
300	7.016	7.023	+0.10
450	7.301	7.292	− .13
500	7.434	7.417	− .23
600	7.675	7.671	− .05
800	8.072	8.072	0
1000	8.356	8.294	− .74
1250	8.621	8.621	0
1500	8.840	8.879	+ .44
1750	9.033	9.079	+ .51
2000	9.208	9.233	+ .27
2500	9.500	9.476	− .25
2750	9.616	9.601	− .16
3000	9.725	9.761	+ .37

As the proof of this paper was being corrected there appeared a paper by **Wohl** and **Magat** [Z. *physik. Chem.*, **19B**, 117 (1932)] on the specific heats and dissociation of gases at high temperatures. Concerning that part of their paper dealing with the specific heat of oxygen, it is noticed that their experimental values are lower than ours. As a matter of fact their values are lower than those calculated from the ordinary Planck–Einstein formula. They attribute this to the incomplete excitation of the oxygen vibrational levels during the time of explosion. On the other hand, our values are higher and they have been well accounted for as outlined in this paper. It may be argued that heat losses would account for our results. This question has been discussed with the exception of possible heat losses through the glass rod ignition system. The surface of the ignition rod is not isolated from the hot gas during the explosion as is the case with the wall of the bomb. It can be shown that in our case the heat loss through the rod is less than 0.02%. This value is arrived at from the slope of the cooling curve immediately following the sharp maximum. From the cooling curve the heat loss after the maximum in a time corresponding to the duration of the explosion is somewhat less than 2%. The surface of the ignition rod is about $^1/_{100}$ the surface of the bomb walls. Not considering the smaller heat conductivity of glass as compared with that of the chromium-plated walls and also the fact that the entire glass rod is not in contact with the hot gases throughout the duration of the explosion, the heat loss through the glass rod is certainly less than 0.02%. This negligible heat loss is in agreement with the findings of Wohl and Magat, who show that only in the case of explosions of hydrogen and oxygen with excess hydrogen but not with excess oxygen is there any appreciable heat loss through the ignition rod. These remarks refer always to explosions in which there is a sharp maximum.

The crucial test is a comparison of explosions at different pressures. Since the heat conductivity of the hot gas is the same at different pressures, the absolute heat loss should be independent of the pressure but the percentage heat loss should be larger in the case of lower pressures and therefore the calculated values of the specific heats should be higher at lower pressures. We find however no influence of pressure on the specific heats.

We are at *a* loss to understand the low values of specific heats obtained by Wohl and Magat unless our explosion times are slightly larger than theirs. However, we hope to repeat that part of Wohl and Magat's work dealing with this subject, in our own apparatus.

Summary

The mean specific heat of oxygen between 300°K. and 1400 to 2500°K. has been determined by exploding ozone–oxygen mixtures in a constant volume bomb. The experimental values after correcting for dissociation are higher than the theoretical values calculated from the known vibrational–rotational levels of the oxygen molecule by an amount which allows one to calculate the energy of the hitherto unknown but predicted $^1\Delta$ metastable level of the neutral oxygen molecule. The $^1\Delta$ level is found to be 0.75 ± 0.05 volt or 17,200 ± 1000 calories above the ground state of the molecule. The new mean specific heat curve of oxygen, which includes the contribution from the $^1\Delta$ level, fits the experimental determinations very well along the whole range of temperatures investigated. It is pointed out that the results also provide a fair proof for the dissociation equation previously proposed by the authors.

A table of true specific heats, C_p, is given from 200°K. to 3000°K. Two empirical formulas have been developed to represent this curve in two different ranges of temperature.

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Ternary Systems. XVII. Sodium Iodide, Potassium Iodide and Water. XVIII. Sodium Iodide, Sodium Iodate and Water[1]

BY ARTHUR E. HILL, HERBERT S. WILLSON AND JOHN A. BISHOP

The relationships of the iodides and iodates of sodium and potassium have interest with respect to the preparation and separation of the salts from the Chilean caliche. The two ternary systems have been studied at three temperatures, with a view to obtaining solubility data and information as to double salt formation.

XVII. SODIUM IODIDE, POTASSIUM IODIDE AND WATER

The salts were of C. P. grade and were in some cases purified by recrystallization until experience showed that no measurable change was obtained. They were dried in an electric oven at 100° to constant weight, in order that complexes of exactly known composition might be made up. The salts were weighed into stoppered Pyres tubes with weighed amounts of water and stirred by mechanical inversion in a water thermostat for periods of a few hours, a time which was shown by analysis to be sufficient for attainment of equilibrium. Small samples of the saturated solution were drawn by suction into a pipet with filtration; one such was dried to constant weight in the oven, while a second was analyzed gravimetrically for total iodide content. With these data the composition with respect to the three components was calculated with of course considerable multiplication of errors because of the indirect determination of sodium and potassium. The composition of the solid phases was determined by algebraic extrapolation of the tie lines through the two points representing the saturated solutions and the original complexes taken.[2] The results are given in Table I.

The solubility of the two pure salts at the three temperatures, obtained by the evaporation of the solutions, cannot with advantage be compared with the figures of the average curves given in the "International Critical Tables,"[3] where the inaccuracy given is ±2%, but a comparison with the recent carefully determined figures of Scott and Frazier[4] and Scott and Durham[5] shows agreement with their direct measurements at 25° within one part in 2000 for the potassium iodide and 1 part in 1600 for the sodium iodide; the agreement with their interpolated curves at 8 and 40° appears

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(1) The material of this paper is from the dissertation of Herbert S. Willson, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University. 1932.

(2) Hill and Ricci. THIS JOURNAL, **53**, 4306 (1931).

(3) "International Critical Tables," 1928, Vol. IV, pp. 235, 239.

(4) Scott and Frazier, *J. Phys. Chem.*, **31**, 459 (1927).

(5) Scott and Durham, *ibid.*, **34**, 1424 (1930).

TABLE I

SYSTEM KI–NAI–H_2O

Temp, °C.	Original complex Wt. % KI	Original complex Wt. % NaI	Saturated solution Wt. % KI	Saturated solution Wt. % NaI	Solid phases
8	...	0.00	57.33	0.00	KI
	46.00	17.40	37.54	19.97	KI
	30.22	35.10	19.20	40.55	KI
	16.71	50.58	8.36	55.58	KI
	9.97	59.90	7.44	57.13	KI + $NaI\cdot 2H_2O$
	5.16	60.12	5.82	58.23	$NaI\cdot 2H_2O$
	3.74	60.99	4.13	59.48	$NaI\cdot 2H_2O$
	0.00	...	0.00	62.49	$NaI\cdot 2H_2O$
25	...	0.00	59.78	0.00	KI
	57.62	7.75	50.32	9.29	KI
	52.57	14.40	42.08	17.60	KI
	56.94	18.88	29.79	30.55	KI
	48.33	26.34	21.43	40.11	KI
	45.32	30.63	15.90	46.91	KI
	36.13	39.14	10.60	54.49	KI
	9.24	61.40	7.59	59.35	KI + $NaI\cdot 2H_2O$
	5.78	64.52	7.06	59.71	$NaI\cdot 2H_2O$
	5.97	63.02	6.80	59.97	$NaI\ 2H_2O$
	4.20	66.31	5.44	60.74	$NaI\cdot 2H_2O$
	3.60	67.09	4.78	61.35	$NaI\cdot 2H_2O$
	1.38	69.42	2.17	63.15	$NaI\cdot 2H_2O$
	0.00	...	0.00	64.72	$NaI\cdot 2H_2O$
40	...	0.00	61.73	0.00	KI
	61.77	9.79	48.04	13.47	KI
	51.27	19.62	35.55	26.20	KI
	36.78	33.77	21.33	42.04	KI
	30.33	44.62	9.68	57.85	KI
	11.47	62.83	7.23	62.34	KI + $NaI\cdot 2H_2O$
	3.21	70.11	4.81	63.92	$NaI\cdot 2H_2O$
	0.00	...	0.00	67.35	$NaI\cdot 2H_2O$

to be equally good. The solid phases at the three temperatures, as shown in Fig. 1, are limited to the compounds potassium iodide and $NaI\cdot 2H_2O$; no double salt is found, and solid solution was not found to occur, within the degree of accuracy of the work. This degree of accuracy, as tested by the method of algebraic extrapolation of tie lines, is doubtless lessened considerably by the use of an indirect method of analysis and the large multiplication of errors which therefore follows. Extrapolations of the tie lines at three temperatures to the composition of the simple salts assumed gave an average variation of 0.88% from the potassium iodide and of 1.46% from the $NaI\cdot 2H_2O$, with no steady drift to the variation; this leaves no doubt as to the identity of the salts, whether or not it is definitive as to the possible occurrence of solid solution within very narrow limits. It will be noted that at the three temperatures used the isothermally invariant point is well over toward the side of the sodium iodide. leaving only a comparatively short solubility curve for that compound.

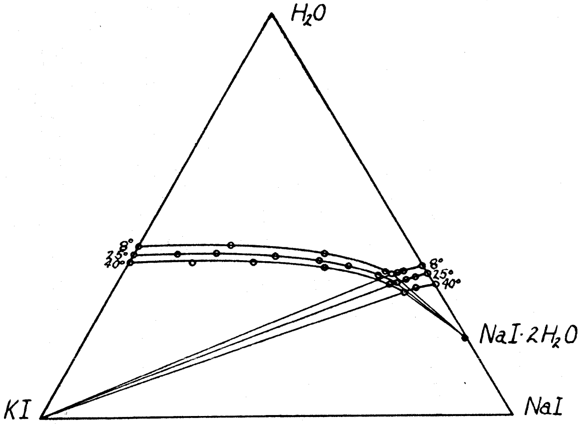

Fig. 1.—The system KI–NaI–H_2O.

XVIII. SODIUM IODIDE, SODIUM IODATE AND WATER

The sodium iodate used in this work was recrystallized from water and dehydrated in an electric oven at 100°. The solubility experiments were conducted as described in the previous section, with the exception that the time given for attainment of equilibrium was from four to seven days. For the analysis, the iodate was determined in a sample by the usual method of iodimetry, thiosulfate being used in the titration. The water was determined in a second sample by evaporation at 100°, the time required for reaching constant weight being about one week. The error brought in during evaporation by oxidation of iodide by iodate was found to be much less than was feared from the color changes which the material showed; it amounted in cases where analysis was made to a loss of only 0.3% of the iodate present, which would affect the figures only in the fourth significant place, and was therefore neglected. During the solubility experiments some slight decomposition, probably photochemical, always took place, as evidenced by the yellow color of the solutions; again, however, analysis showed that the iodine set free amounted to only a few thousandths of one per cent., a wholly negligible amount. The results of the experiments are given in Table II.

Algebraic extrapolation of tie lines through the points showed fairly good concordance; in only four cases is the variation from the true composition more than 1%.

The above figures, when plotted as shown in Figs. 2, 3 and 4, indicate two points of some interest with respect to the system. The first is that the solubility of the iodate is very greatly decreased by the presence of iodide, falling at the saturation point to as low as 0.02% at 8°, and rising

TABLE II

SYSTEM $NaIO_3$–NaI–H_2O

S.S. = solid solution.

Temp, °C.	Original complex		Saturated solution		Density	Solid phases
	Wt % NaI	Wt. % $NaIO_3$	Wt % NaI	Wt. % $NaIO_3$		
8	0.00	...	0.00	3.89	1.035	$NaIO_3 \cdot 5H_2O$
	5.85	4.39	6.05	1.99	1.069	$NaIO_3 \cdot 5H_2O$
	15.08	9.79	17.18	1.44	1.169	$NaIO_3$ $5H_2O$
	19.67	10.33	19.47	1.84	1.196	$NaIO_3 \cdot 5H_2O$ + S S.
	27.60	13.42	25.20	0.72	1.249	S.S.
	40.01	5.07	40.70	.08	1.445	S.S.
	55.44	4.53	57.87	.02		S.S.
	61.58	5.03	62.44	.02	1.861	S.S. + $NaI \cdot 2H_2O$
	...	0.00	62.49	.00	...	$NaI \cdot 2H_2O$
25	0.00	...	0.00	8.67	1.077	$NaIO_3 \cdot H_2O$
	9.93	16.16	11.57	4.23	1.107	$NaIO_3 \cdot H_2O$
	20.99	15.94	24.54	2.68	1.253	$NaIO_3 \cdot H_2O$
	26.86	8.37	28.70	2.48	1.290	$NaIO_3 \cdot H_2O$
	31.25	3.73	31.72	2.41	1.340	$NaIO_3 \cdot H_2O$
	30.32	6.07	31.74	2.36	1.340	$NaIO_3 \cdot H_2O$
	31.24	7.03	31.99	2.36	1.341	$NaIO_3 \cdot H_2O$ + S.S.
	33.03	7.79	33.04	2.04	1.352	S.S.
	36.56	9.09	36.64	1.22	1.377	S.S.
	45.03	5.03	46.08	0.31	...	S.S.
	52.62	9.37	56.83	.17	1.722	S.S.
	67.58	2.34	64.67	.08		S.S. + $NaI \cdot 2H_2O$
	...	0.00	64.72	.00		$NaI \cdot 2H_2O$
40	...	0.00	0.00	11.70		$NaIO_3 \cdot H_2O$
	15.00	7.15	15.33	5.24		$NaIO_3 \cdot H_2O$
	16.96	10.54	18.16	4.74		$NaIO_3 \cdot H_2O$
	19.23	6.49	19.64	4.47		$NaIO_3 \cdot H_2O$
	21.03	8.02	22.06	3.90		$NaIO_3 \cdot H_2O$
	26.42	5.09	26.85	3.49		$NaIO_3$
	31.78	8.30	33.65	2.92		$NaIO_3$
	39.84	4.35	40.52	2.78		$NaIO_3$
	39.00	9.97	41.16	2.79		$NaIO_3$ + S.S.
	39.91	9.99	41.30	2.80		S.S.
	40.00	17.14	42.55	2.72		S.S.
	50.31	5.43	51.97	0.58		S.S.
	62.00	4.00	64.40	.47		S.S.
	63.96	4.00	66.15	.32		S.S.
			67.58	.28		S.S. + $NaI \cdot 2H_2O$
			67.35	.00		$NaI \cdot 2H_2O$

only to **0.3%** at 40°. This indicates that sodium iodide can be freed from iodate by recrystallization only with difficulty and only when the initial iodate concentration is lower than the above figures, which may well be the explanation of the very frequent appearance of iodate as impurity in commercial iodide, if the source of the material is such as would contain iodate. It will be shown in a later publication that this condition does not occur in the system containing the two corresponding potassium salts, which may be the reason that the potassium iodide quite regularly has a higher degree of purity than the sodium salt.

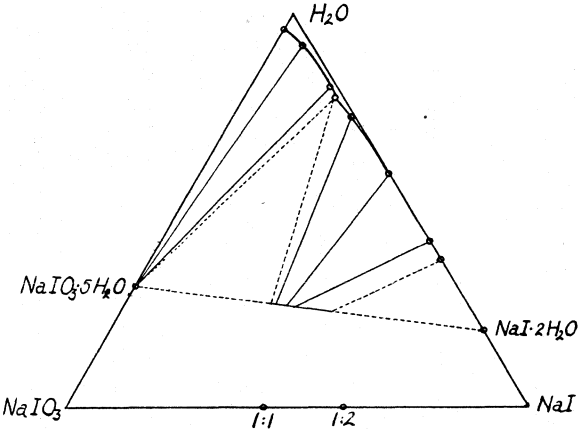

Fig. 2.—8° Isotherm: $NaIO_3$–NaI–H_2O.

The second point of interest is the occurrence of a new complex iodide–iodate, which was found at all three temperatures and which is the saturating phase over a considerable part of the entire range of concentrations. This was found to be not a double salt, but a solid solution of the two hydrated salts $NaIO_3{\cdot}5H_2O$ and $NaI{\cdot}2H_2O$. The evidence lies not merely in the failure of the tie lines to intersect with any reasonable constancy at a single point, but also in the isolation and analysis of the solid phase. For this test the ordinary method of filtration and analysis offered difficulty,

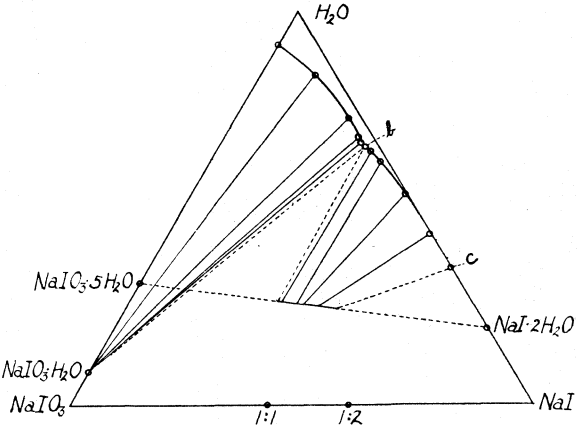

Fig. 3.—25° Isotherm: $NaIO_3$–NaI–H_2O.

for the solid obtained from the solubility experiments was very finely divided and carried a large percentage of highly concentrated solution upon its surface, making a very large correction necessary. To avoid this condition, crystals were slowly grown from a solution made up in the area of undersaturation above the line *b-c* (Fig. **3**) by evaporation over sulfuric acid at room temperatures. The crystals thus obtained were well formed and several millimeters in diameter, and could be quickly centrifuged to a condition of superficial dryness so that they ran easily on the glass of a test-tube with no evidence of stickiness; it is quite certain that they could not have contained more than very small amounts of solution. The results of their analysis are given in the first two columns of Table III.

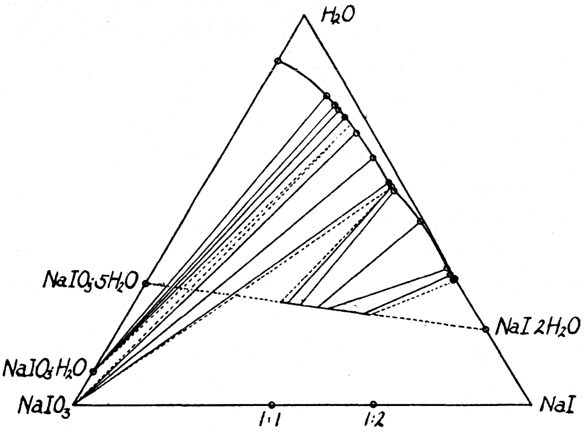

Fig. 4.—40° Isotherm: $NaIO_3$–NaI–H_2O.

TABLE III

ANALYSIS OF SOLID SOLUTIONS

	I	II	III
Wt. % $NaIO_3$	33.24	30.31	35.6
Wt. % NaI	38.09	44.41	40.2

These first two points will be found to represent quite different compositions, and to fall fairly close to the line drawn as representing the series of solid solutions. The third analysis represents a sample taken directly from a solubility experiment and filtered rapidly; it was put to dry in a desiccator containing a partially dehydrated mixture of $NaIO_3{\cdot}H_2O$ and $NaI{\cdot}2H_2O$. In two months time it lost 14.64% of water and reached a constant weight which remained unchanged for seven months. The analysis of the solution from which it was formed being known, the necessary correction[6] was made in the analysis of the solid; the corrected analysis, shown in the third column, also falls close to the expected line.

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(6) Hill, THIS JOURNAL, 52, 3828 (1930).

The wide variation in the composition of the three samples is convincing evidence of solid solution. The position of the three points is sufficiently close to the line joining the composition of $NaI \cdot 2H_2O$ and $NaIO_3 \cdot 5H_2O$ to indicate that these are the solids entering into the solid solution. That this should be the case at the lower temperature is in no wise striking; but that it should also be so at 40°, some 20° above the transition temperature of $NaIO_3 \cdot 5H_2O$[7] involves the conclusion that the vapor tension of $NaIO_3 \cdot 5H_2O$ in the solid solution is considerably reduced by the presence of the $NaI \cdot 2H_2O$ in the same molecule.

It will be noted that the area of solid solutions begins quite close to the ratio of 1:1 for the two salts, corresponding to the formula of a comparatively simple double salt, $NaIO_3 \cdot NaI \cdot 7H_2O$, and extends with increase in the amount of iodide to a point near to or at the 1:2 ratio, $NaIO_3 \cdot 2NaI \cdot 9H_2O$. This approximation of solid solution to the composition of stoichiometrical ratios, well known in the case of glaserite, has been noted in a number of interesting cases.[8] In commenting upon these, Timmermans[9] remarks that they may possibly be regarded as examples of Berthollidean compounds of variable composition as opposed to Daltonian compounds of fixed composition. Without committing one's self to any fundamental theory in the matter, one is obliged to note the frequency with which such solid solutions approximate the stoichiometrical ratios, and to suspect that doubtless certain substances have been reported as compounds on this basis whereas they are truly solid solutions.

Summary

1. The system $NaI-KI-H_2O$ has been studied at 8, 25 and 40°; no compound formation occurs.

2. The system $NaIO_3-NaI-H_2O$ has been studied at the same three temperatures; at all of these there exists, over a wide range of liquid concentration, a series of solid solutions of the composition $(NaIO_3 \cdot 5H_2O)_n \cdot (NaI \cdot 2H_2O)_m$, beginning at the 1:1 ratio and extending to approximately the 1:2 ratio.

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[7] Foote and Vance, Am. J. *Sci.*, 16, 68 (1928); 18, 375 (1929); Hill and Donovan, THIS JOURNAL, 63, 934 (1931).

[8] Kurnakow, *Z. anorg. Chem*., 88, 109 (1914); Foote and Saxton, THIS JOURNAL, 36, 1695 (1914); Clendennin and Rivett, *J. Chem. Soc.*, 119, 1329 (1921).

[9] Timmermans, "La Notion d'Espèce en Chimie," Paris, 1928, p. 16.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

X-Ray Studies of the System Nickel–Oxygen–Water. I. Nickelous Oxide and Hydroxide[1]

BY R. W. CAIRNS AND EMIL OTT

Introduction

Numerous investigators[2] have made x-ray studies of natural and artificial nickelous oxide. The crystal structure has been definitely established as face centered cubic, with a lattice spacing approximately 4.17 Å. The most accurate determinations are probably those of Brentano[3] (4.1705 Å.) and Ksanda[4] (4.171 ± 0.003 Å.). Since both determinations were made with the use of sodium chloride diffraction as a primary standard, there is little doubt as to their accuracy.

There appear in the literature several reports of ostensibly new modifications of NiO. Lachand and Lepierre[5] reported that the oxides prepared by ignition of what they believed to be two crystalline modifications of anhydrous nickel sulfate retained the external crystal form of the sulfates. The densities of the two oxides which they prepared were 6.67 g. per cc. and 6.70 g. per cc., as compared with a density of 6.80 g. per cc. calculated from x-ray data.

Hedvall[6] found that NiO which had been repeatedly heated to 1000° for several hours in molten potassium chloride possessed a density of 7.45 g. per cc. Since this value is considerably higher than the density calculated from x-ray data of the normal form, it would appear that a new modification was present, and it has been treated as such in at least one instance.[7]

Prasad and Tendulkar[8] have investigated the variation in physical properties, as influenced by temperature of preparation, of samples of NiO prepared by heating nickel nitrate, hydroxide and basic carbonate at temperatures of 400 to 1000°. The oxide obtained at 400° was black and the one at 1000° green. They found that the density and electrical resistance increased, and the rate of solution in sulfuric acid decreased as the temperature of preparation was raised. They concluded that there were two forms of NiO, the black form prepared at 400° and the greenish-gray form, at 1000°. The changes in properties were attributed to changes

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(1) From a thesis submitted by Robert W. Cairns in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Davey and Hoffman, *Phys. Rev.*, 16, 333 (1920); Davey, *ibid.*, 17, 402 (1921); Clark, Asbury and Wick, THIS JOURNAL, 47, 2661 (1925); Lunde, *Z. anorg. allgem. Chem.*, 163, 345 (1927); Hendricks, Jefferson and Schultz, *Z. Kryst.*, 73, 376 (1930).

(3) Brentano, *Proc. Roy. Soc.* (London), 37, 184 (1925); *Phil. Mag.*, [7] 3, 413 (1927).

(4) Ksanda, *Am. J. Sci.*, **22**, 131 (1931).

(5) Lachand and Lepierre, *Bull. soc. chim.*, [3] 7, 600 (1892).

(6) Hedvall, *Z. anorg. allgem. Chem.*, **92**, 382 (1915).

(7) *See* Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5 Auflage, I, p. 304 (1923).

(8) Prasad and Tendulkar, *J. Chem. Soc.*, 1403 (1931).

(1) in particle size, (2) from amorphous to crystalline state, (3) in crystalline form and (4) of an intramolecular nature.

Leblanc and Sachse[9] have shown that the oxide prepared by the same method at 400 to 500° possessed the normal cubic structure of the high-temperature preparation as evidenced by the x-ray diffraction pattern. They have also proved that the black color was due to traces of active oxygen.

Further, a new modification of nickel oxide was reported by Bennett, Cairns and Ott[10] but further work has shown that the reported results were erroneous. The substance then reported as NiO by Dr. Bennett[11] was subsequently found by us to contain active oxygen and water in bound form. That the diffraction pattern appeared in the first approximation to fit a cubic structure, was purely accidental. A search of the literature revealed no other reports of different modifications of nickelous oxide.

Inasmuch as there has been no x-ray evidence to disprove or substantiate the existence of the different modifications as reported, the present investigation was undertaken. Incidental to this work more accurate data were obtained on the crystal structure of nickelous hydroxide. The crystal structure of nickelous hydroxide has previously been determined by Natta.[12] The lattice type was found to be hexagonal with one molecule per unit cell. The lattice constants as determined by the x-ray diffraction were $a_0 = 3.07$ Å. and $c_0 = 4.61$ Å.

Nickelous hydroxide as generally prepared by precipitation from nickel salt solutions contains, after drying, more water than is necessary for a composition of $Ni(OH)_2$. In some cases this has been taken as evidence of the formation of definite hydrates.[13]

Experimental Part

Preparation of Samples

Nickel Oxides from Sulfates.—Twenty grams of ammonium bisulfate and ten grams of nickel sulfate hexahydrate were fused together in a porcelain crucible. The bisulfate was volatilized by heating the mass to red heat for four hours. The residue of crystalline anhydrous nickel sulfate was found by microscopic examination to be in the form of yellow-green transparent octahedra. In a second preparation, the same procedure was followed except that 3 g. of concd. sulfuric acid was added to the mixed sulfates before fusion. The sulfate product in this case crystallized in lens-shaped crystals. x-Ray powder pictures of the two sulfates were identical, and their complexity indicated low symmetry for the crystal structure. Thus the two forms of nickelous sulfate do not represent two different modifications, but are merely different habits.

Each of the two preparations of nickel sulfate was heated at white heat in a platinum crucible for an hour. The oxide products were moss-green in color and retained the external form of the original sulfates.

Pure Nickelous Oxide from the Nitrate.—C. P. nickel nitrate was twice recrystal-

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(9) Leblanc and Sachse, Z. *Elektrochcm.*, **32**, 204 (1926).

(10) Bennett, Cairns and Ott, THIS JOURNAL, **53**, 1179 (1931).

(11) Bennett, Dissertation, Johns Hopkins University, 1930.

(12) Natta. *Gazz. chim. ital.*, **58**, 344 (1928).

(13) See Gmelin-Kraut, "Handbuch der anorg. Chem." Vol. 1, pp. 43-44 (1909).

ized from water. The nitrate initially gave a very faint test for cobalt by Vogel's method, but this was negative after one recrystallization. The purified nitrate was heated to white heat in a platinum crucible. A surface layer of dark colored oxide was formed due to contact with air, but beneath this the pure NiO was yellow-green and gave no test for active oxygen by the Bunsen method.

The purified nitrate was also treated in solution with ammonia gas, and the precipitated hexammoniate was further recrystallized twice from strong ammonia solution. The product was ignited in nitrogen in an electric furnace at 1000°. The oxide thus formed was also green and contained no active oxygen.

Nickelous Oxide by Hedvali's Method.—Pure NiO was heated in molten potassium chioride at white heat over a period of five hours. The heating was momentarily interrupted every half hour and the mass allowed to cool for five minutes. At the conclusion of the heating the potassium chloride was leached out with water and the light green oxide filtered off and washed.

Nickelous Oxide by Decomposition of Nickelic Oxide Hydrate.—A sample of nickelic oxide-hydrate, the approximate composition of which was $Ni_2O_3 \, 2H_2O$ (see following paper), was heated for three days at 120°. The black color remained although only a trace of active oxygen was present. The same oxide-hydrate was heated in nitrogen at 1000" for two hours. The green product thus formed contained no active oxygen.

Nickelous Hydroxide.—A solution of 25 g. of potassium hydroxide in 250 cc. of water was added dropwise to a solution of 60 g. of $Ni(NO_3)_2 \, 6H_2O$ in 500 cc. of water at room temperature The precipitation was carried out with rapid stirring in a closed three-necked flask of three liters capacity. Carbon dioxide-free air was kept over the solution. After precipitation the product was washed by decantation three times, in a cylinder of ten liters capacity. The cylinder was kept covered with a ground-glass plate except during decantation. A minimum time of exposure to air was allowed, and carbon dioxide-free water was used in the decantation. After the supernatant liquid had been removed in the last decantation, the precipitate was filtered with suction on a covered Buchner filter. After washing, the product was dried in a desiccator for two weeks over concd. sulfuric acid.

The preparation was repeated with the nitrate solution kept at 100" during precipitation. The final composition of this product, after drying in *vacuo* over calcium chloride for a day, was $NiO \, 1.21H_2O$, as shown by nickel and water analyses. The product contained 0 6% of carbon dioxide. Another preparation was carried out at 0°, and the product was kept in the wet state for x-ray investigation.

Method of x-Ray Analyses.—The source of x-rays was a hot filament metal tube with a copper anticathode (model Dr. Seeman, Freiburg). The tube was operated at *ca.* 20 kilovolts and 30–40 milliamperes. Nickel foil was used for practically complete absorption of Kg-radiation. The radiation was occasionally checked spectroscopically and found to be CuK_α essentially. The camera was of the Debye–Scherrer type (Dr. Leiss, Berlin-Steglitz) with an effective diameter of 114 6 mm The powdered samples were contained in thin collodion tubes of 0.5 mm. diameter. In the accurate determinations the samples were powdered in an agate mortar with equal parts of Kahlbaum "sodium chloride for analysis." The diffraction of sodium chloride thus appeared on the films and was used as a standard in measurement of the diffraction of the nickel compounds. The values of sin Θ for the glancing angles for sodium chloride were first determined from microcomparator measurements of the line spacings on the films and the known diameter of the camera. These values were then compared with the values calculated assuming $a_0 = 5.628$ **Å.** for chemically pure sodium chloride. A plot of these corrections against the values of sin Θ, uncorrected, was used to determine the corrections to the observed sines of the glancing angles for NiO and $Ni(OH)_2$.

Some of the diagrams obtained may be found in a following paper.

Results of x-Ray Analysis

Nickelous Oxide.—The two samples of nickel oxide prepared by ignition of the sulfates gave x-ray diffractions corresponding to the usual face-centered type of crystal. There was no distortion of the lattice within the limits of experimental error. It was evident that the oxides were merely pseudomorphic with the original sulfates.

TABLE I

NiO FROM $Ni(NO_3)_2\ 6H_2O$

Compound	Miller indices	Sin Θ obs.	Sin 8 corr.	a_0 for NiO, Å.
NaCl	200	0.27626	0.27363	....
NiO	111	.32227	.31992	4.1688
NiO	200	.37156	.36956	4.1671
NaCl	220	.38873	.38697	
NaCl	222	.47533	.47393	....
NiO	220	.52362	.52258	4.1674
NaCl	400	.54801	.54726	....
NiO	311	.61291	.61242	4.1699
NiO	222	.64026	.63994	4.1681
NaCl	422	.67075	.67025	....
NiO	400	.73875	.73905	4.1675
NaCl	440	,77375	.77393	....
NiO	331	.80412	.80482	4.1702
NaCl	442	.81991	.82089	....
NiO	420	.82511	.82595	4.1691
NaCl	620	.86410	.86530	....

Average value for a_0 for NiO = 4.1685

Average deviation from the mean for a_0 = 0.0008

TABLE II

NiO FROM $Ni(NO_3)_2{\cdot}6NH_3$

Compound	Miller indices	Sin Θ obs.	Sin Θ corr.	a_0 for NiO, Å
NaCl	200	0.27607	0.27363	....
NiO	111	.32207	.32100	4.1677
NiO	200	.37118	.36947	4.1681
NaCl	220	.38854	.38697	
NaCl	222	.47486	.47393	....
NiO	220	.52324	.52269	4.1666
NaCl	400	.54756	.54726	....
NiO	311	.61257	.61249	4.1695
NiO	222	.63978	.63983	4.1688
NaCl	422	.67043	.67025	....
NiO	400	.73846	.73896	4.1680
NaCl	440	.77329	.77393	....
NiO	331	.80412	.80490	4.1699
NaCl	442	.82015	.82089	....
NiO	420	.82536	.82616	4.1681
NaCl	620	.86427	.86530	....

Average value for a_0 for NiO = 4.1683

Average deviation from the mean for a_0 = 0.0008

Data on the x-ray diffractions of the two samples prepared from nickel nitrate hexahydrate and hexammoniate are given in Table I and Table II.

The average of these two determinations was then 4.1684 Å. In consideration of the accuracy possible through use of sodium chloride as a primary standard and, because of the purity of the samples, this value is probably accurate to 0.001 Å.

By an identical determination the nickelous oxide prepared by Hedvall's method was found to have the lattice constant, $a_0 = 4.1665$ Å. The average deviation from the mean value for a_0 was in this case 0.0007 Å. Thus this value is identical with the above ones within the experimental error (± 0.001). Hence it appears that Hedvall's density determination was subject to error, as an experimental density of 7.45 g. per cc. would require a lattice spacing of 4.04 Å. or less.

The two samples of nickelous oxide prepared by decomposition of nickelic oxide hydrate at 120 and 1000° possessed identical crystal diffraction, with the exception that the diffraction lines of the low temperature preparation were exceedingly diffuse, while those of the sample ignited at 1000° were very sharp. The differences in properties observed by Prasad and Tendulkar[5] could all be explained on the basis of a difference in particle size. The black color was caused by traces of active oxygen.

TABLE III

$Ni(OH)_2$ PRECIPITATED AT 100°

hkl	Sin θ obs.	Sin θ corr.	$\sin^2\theta$ corr.	$\sin^2\theta$ calcd.
001	0.17021	0.16676	0.02781	0.02794
100	.28736	.28501	.08123	.08152
101 002	.33258	.33065	.10933	.10946 .11176
102	.44072	.43980	.19342	.19329
110 003	.49470	.49428	.24431	.24457 .25147
111	.52139	.52121	.27166	.27251
200	.57071	.57100	.32604	.32610
103	.57715	.57749	.33349	.33299
201 112	.59377	.59428	.35357	.35404 .35634
202 004	.66066	.66178	.43795	.43783 .44706

$a_0 = 3.114$ Å.; $c_0 = 4.617$ Å.; $c/a = 1.483$

NaCl Diffraction

hkl	Sin θ obs.	Sin θ calcd.
200	0.27620	0.27363
220	.38832	.38697
222	.47460	.47393
400	.54683	.54726
420	.61130	.61185
422	.66913	.67025

Nickelous Hydroxide.—The room temperature preparation gave a very diffuse x-ray diffraction pattern with the innermost line (corresponding to the (001) spacing)[14] a very broad band. The preparation made at 100° gave much sharper diffraction lines and all of the inner lines were clear enough for accurate measurement with a millimeter rule. The diffraction pattern corresponded to that of a crystal of hexagonal lattice type. Data are given in Table III.

The average deviation between the values of $\sin^2 \Theta$ observed and $\sin^2 \Theta$ calculated from the quadratic formula for the hexagonal system was 0.18%, with the values of the lattice constants $a_0 = 3.114$ Å. and $c_0 = 4.617$ Å. A second determination gave agreement to 0.28%. Our more accurate value for a_0 differs by *ca.* 1% from Natta's.[12]

The calculated density was 3.94 g. per cc. for one molecule per unit cell, in fair agreement with a determined density of 3.56 g. per cc., the discrepancy being due probably to adhering air and water.

Expressed on rhombohedral axes the unit cell contained three molecules per unit cell, showing that the hexagonal type was the simplest structure.

In a previous determination[12] the structure was assumed to be of the cadmium iodide type, with the atoms of $Ni(OH)_2$ at the following positions of D^3_{3d}: Ni at 0, 0, 0; OH at $^1/_3$, $^2/_3$, u; $^2/_3$, $^1/_2$, $\bar{u}$. The optimum value of u was found to be 0.25.

In this work the atomic positions were assumed to be the above, and the relative intensities of the planar reflections were computed from the formula

$$I \propto \frac{1+\cos^2 2\Theta}{\sin^2\Theta\cos\Theta}\cdot j\cdot\left(F_{\mathrm{Ni}} + F_{\mathrm{O}}\cos 2\pi\left(\frac{h+2k}{3}+ul\right)\right)^2$$

where j is the heaping factor[15] for the plane (h k l) and F_{Ni} and F_{O} are the atomic reflecting powers for Ni and O atoms.[16]

TABLE IV

$Ni(OH)_2$

$h\,k\,l$	Observed intensity	Calculated intensity $u = 0.23$	0.25	0.27
001	Very strong	93	79	65
100	Medium strong	25	25	25
101	Very strong	50	49	47
102	Medium strong	18	23	28
110	Medium strong	22	23	25
111	Medium weak	8	7	6
200	Very weak	5	5	5
103	Very weak	5.5	5	5
201	Medium weak	7	7	7
202	Medium weak	6	5.5	4.5

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(14) It is of interest to note that this important spacing was not directly observed in the previous work of Natta.

(15) Schleede and Schneider, "Röntgenspektroskopie und Kristallstrukturanalyse," Rand II, p 250, Table 33, Berlin, 1929.

(16) Wyckoff, Phyr. *Rev.*, **35**, 583 (1930).

The intensities, in arbitrary units, for different values of the parameter u are given in Table IV. The best agreement with observed intensities was found for $u = 0.25$, confirming Natta's results.

The x-ray diffraction of a wet, freshly precipitated sample of $Ni(OH)_2$ prepared at 0° showed a very diffuse diffraction in which all the lines corresponded to the strongest reflections of the dry material. No evidence could be found of any definite hydrates of $Ni(OH)_2$.

A sample of NiO, obtained by decomposition of $Ni(OH)_2$ in nitrogen at 500°, showed no change in its x-ray diffraction after the material had been heated in a bomb tube in water at 150° for five days. Hiittig and Peter[17] have found that nickelous hydroxide cannot be formed by action of water at room temperature on NiO. Thus it appears that the decomposition of nickelous hydroxide to the oxide is not reversible under ordinary pressures.

Summary

1. It has been found that several new modifications of nickelous oxide reported in the literature conform to the usual face-centered type of lattice. The lattice constant for preparations made according to the methods described did not vary from the accepted value for the normal form of the oxide, within the limits of experimental error.

2. The lattice constant of pure NiO has been redetermined more accurately using pure sodium chloride as a reference substance. The value as determined for two different preparations of nickelous oxide was

$$a_0 = 4.1684 \pm 0.001 \text{ Å}.$$

3. It has been possible to redetermine the lattice constants of hexagonal $Ni(OH)_2$ with greater accuracy than heretofore. The lattice constants were found to be $a_0 = 3.114 \pm 0.005$ Å. and $c_0 = 4.167 \pm 0.005$ Å. Intensity calculations indicated that the crystal had the symmetry of the space group D^3_{3d}, with the following atomic coördinates: Ni at (0, 0, 0); OH at ($^1/_3$, $^2/_3$, 0.25), ($^2/_3$, $^1/_3$, -0.25), in accordance with a previously reported structure determination.

4. The reported existence of hydrates of $Ni(OH)_2$ has been disproved.

5. Two crystal forms of nickel sulfate, previously thought to be different modifications, were found to be identical, differing only in crystalline habit. The nickel oxides prepared from the sulfates were merely pseudomorphic with them, and do not represent new modifications.

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(17) Huttig and Peter, *Z anorg. allgem. Chem.*, **189**, 184 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

X-Ray Studies of the System Nickel–Oxygen–Water. II. Compounds Containing Trivalent Nickel[1]

BY R. W. CAIRNS AND EMIL OTT

Introduction

The chemistry of the oxides of nickel and their hydrates has been a controversial subject for a great many years. A number of higher oxides of nickel have been reported, but there has followed positive proof that such oxides do not exist. Wohler and Balz,[2] Baubigny,[3] Rose,[4] Glaser,[5] Moissan,[6] Vaubel,[7] Lunde,[8] and Clark, Asbury and Wick[9] have reported preparations of oxides such as Ni_3O_4, Ni_2O_3 and NiO_2. For the most part the compounds were analyzed for their nickel content alone and the oxygen content determined on this basis. The general methods of preparation in use involved the dry heating of nickel compounds such as the hydroxide, oxide, nitrate, chloride or basic carbonate in air or oxygen, at temperatures of 200 to 500°. Subsequent work by Leblanc and Sachse[10] has shown the above work to be erroneous. The latter made preparations of the black oxide of nickel according to the above methods, and analyzed the products completely, for nickel, active oxygen and water. In all cases, the active oxygen content was very low, corresponding to less than 10% of Ni_2O_3. The errors in the previous results were due to the fact that the water contents were not taken into account. Leblanc and Sachse therefore assumed that the black oxide of nickel, as prepared in the above ways, was not a homogeneous higher oxide of nickel, but was a system of nickelous oxide, active oxygen and water, containing less than ten per cent. of higher oxides. x-Ray diagrams of their products showed only the diffraction lines for NiO. Their work was substantiated by Hendricks, Jefferson and Schultz[11] who were unable to obtain anything but nickelous oxide with traces of active oxygen, by any of the above methods.

It appears quite clear that anhydrous higher oxides of nickel do not exist. However, there remains for consideration another class of nickel compounds containing active oxygen, prepared by quite different methods. These compounds have been previously referred to as higher oxides or oxide-hydrates. The general method of preparation has been oxidation

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(1) From a thesis submitted by Robert W. Cairns in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Wohler and Balz, Z. *Elektrochem.*, 27, 406 (1921).

(3) Baubigny, *Compt. rend.*, 87, 1082 (1878); 141, 1232 (1905).

(4) Rose, Pogg. *Ann.*, 84, 571 (1851).

(5) Glaser, *Z. anorg. Chem.*, 36, 1 (1903).

(6) Moissan, *Ann. chim. phys.*, [5] 21, 239 (1880).

(7) Vaubel, *Chem. Z.*, 46, 978 (1922).

(8) Lunde, *Z. anorg. allgem. Chem.*, 163, 352 (1927).

(9) Clark, Asbury and Wick, THIS JOURNAL, 47, 2661 (1925).

(10) Leblanc and Sachse, Z. *Elektrochem.*, 32, 59 and 204 (1926).

(11) Hendricks, Jefferson and Schultz, Z. *Kryst.*, 73, *376* (1930).

of nickel salt solutions by basic solutions of oxidizing agents such as bromine, chlorine and persulfates. Belluci and Clavari[12] made a series of preparations, using different oxidizing agents and various temperatures of preparation. The products were analyzed for active oxygen and nickel. They computed the Ni:O ratios from the data and found the values to range from 1:1.3 to 1:1.9, the oxidation taking place to the greatest extent at a temperature of precipitation of 0°. They obtained no definite evidence of the existence of an intermediate oxidation product such as Ni_2O_3, and therefore assumed the products to be mixtures of NiO and NiO_2. No attempt was made to determine the water content of the products, or to find whether this was bound or simply adsorbed. Clark and co-workers[9] reported the preparation of $NiO_2 \cdot xH_2O$ by the same method, and found the product to be amorphous, giving no x-ray diffraction pattern. Howell[13] studied the decomposition of the precipitates formed when basic solutions of chlorine were added to nickel sulfate solutions. The products were instable in suspension at 100°, losing active oxygen fairly rapidly. Howell determined the Ni:O ratios in the manner described above. Initial values for this ratio reached 1:1.65, and approached 1:1 for precipitates decomposed at 100°. There was a rapid initial loss of about 25% of the active oxygen, followed by a more gradual loss of the remainder. He interpreted the results to indicate that two higher oxides were present, NiO_2, which was very instable and accounted for the rapid initial loss of active oxygen, and Ni_2O_3, which lost active oxygen much less rapidly. He made no mention of the possibility that the products might contain bound water.

Hüttig and Peter[14] studied the system nickelic oxide–water. Products prepared by the method of Belluci and by oxidation of suspended nickelous hydroxide had compositions expressible as $Ni_2O_3 \cdot 3\text{–}4H_2O$. The Ni:O ratios were exactly 1:1.5, but the water contents varied with conditions of drying. By the isobaric decomposition of the products at temperatures of 100 to 140° and a total pressure of about 10 mm. they believed to have found evidence for the existence of a monohydrate of Ni_2O_3. They also found that the composition of the product obtained by heating the above preparations in water at 200° was approximately $Ni_2O_3 \cdot H_2O$. x-Ray diagrams of the first two products and of the product of the water heating were obtained. No correspondence between any of the patterns was noticeable. They assumed the latter pattern to be characteristic of the monohydrate of Ni_2O_3, but did not succeed in placing any interpretation on the x-ray results on the original products, other than to suggest that a trihydrate might exist. No evidence of such a compound was indicated in the isobaric decomposition experiments. They found the water con-

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(12) Belluci and Clavari, *Gazz. chim. ital.*, **36**, 58 (1906); **37**, 409 (1907).

(13) Howell, *J. Chem. Soc.*, **123**, 669 and 1772 (1923).

(14) Hüttig and Peter, *Z. anorg. allgem. Chem.*, **189**, 190 (1930).

tents of the products to be completely reversible at temperatures below 138°, at which temperature the composition of the residue-became $Ni_2O_3\cdot H_2O$. At temperatures above this irreversible decomposition took place according to the equation

$$2(Ni_2O_3\cdot H_2O) \longrightarrow 4NiO + 2H_2O + O_2$$

Leblanc and R. Müller[15] published a thesis which we received after completion of our work in which they study the system of higher nickel oxides and water. Their attempted x-ray study was unsuccessful, due to experimental reasons. They were able to obtain preparations giving a Ni:O ratio as high as 1.75. The isothermic decomposition gave no evidence of any definite oxides or hydrates in strong contrast to the findings of Hüttig and Peter.[15] It is also our conviction that the results of the latter authors were accidental.

Experimental Part

Chemical Analyses.—Nickel was determined electrolytically. Samples were dissolved in very dilute sulfuric acid to avoid loss in spray caused by rapid evolution of oxygen. After electrolysis solutions were tested with hydrogen sulfide to assure that all nickel was recovered.

Active oxygen was determined by a modified Bunsen method, using an apparatus described by Gooch.[16] Samples were dissolved in dilute hydrochloric acid. The chlorine evolved was swept into potassium iodide solution with carbon dioxide, while the acid solution was gently boiled. The free iodine was titrated with thiosulfate.

Water and carbon dioxide were determined by heating the samples in a quartz tube in an electric furnace at about 1000". The vapors were swept into absorption tubes by a stream of purified nitrogen. The carbon dioxide contents were approximately 0.5% for all materials analyzed in this work.

x-Ray Analyses.— The method was identical with the one in our previous article.[17]

The powder pictures thus obtained were measured with a millimeter rule. Since diffraction lines in all cases were rather broad it was not feasible to use a micro-comparator. The x-ray data recorded in the report include the linear distances between corresponding lines on each side of the film, and the estimated relative intensities of the diffraction lines.

Preparation of Samples.—A. A solution of 55 g. of potassium hydroxide and 12 cc. of bromine in 500 cc. of water was added dropwise to a solution of 100 g. of $Ni(NO_3)_2\cdot 6H_2O$ in 1500 cc. of water, with rapid stirring. Precipitation was carried out in absence of carbon dioxide as described in the preceding article.'' The temperature of precipitation was 25°. The precipitate was washed five times by decantation, then filtered and washed thoroughly on the filter, as described in the preparation of nickelous hydroxide. The product was dried over concentrated sulfuric acid for a few days and then over 1:1 sulfuric acid for two weeks. The final analysis corresponded to the composition $Ni_2O_3\cdot 3.19H_2O$ (Ni_2O_3 73.5%, H_2O 25.7%, CO_2 0.5%). This preparation was designated as product A.

The product A was dried more thoroughly at various temperatures: (1) in a vacuum desiccator over calcium chloride, at about 1 mm. pressure, (2) in an electric oven in air,

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[15] R. Müller, Dissertation, Leipzig, 1931.

[16] Gooch, "Representative Procedures in Quantitative Analysis," John Wiley and Sons, Inc , New York, 1916, p. 187.

[17] Cairns and Ott, THIS JOURNAL, 55, 627 (1933).

and **(3)** in **a** metal tube under 10 atmospheres of oxygen, with phosphorus pentoxide present to absorb water. Analyses of products are given in the following table.

Method of drying	Temp., °C.	Time of drying	% Ni_2O_3	% H_2O	% NiO by diff.	$NiO_2O_3:H_2O$ mol. ratio
(1)	25	3 days	80.8	17.3	1.9	1:1.97
(2)	130	24 hours	41.3	9.7	49.0	1:2.16
(3)	320	20 hours	30.7	8.8	60.5	1:2.65

The x-ray diagrams of product A and of the product dried by method **(1)** were identical. Data are given in Table I, 1, and Fig. 1A. The products dried by methods (2) and (3) gave only lines for NiO (see Table 1, 4, and Fig 1B) the decomposition probably destroying the crystallinity of the undecomposed portion. No other foreign diffractionlines were observed

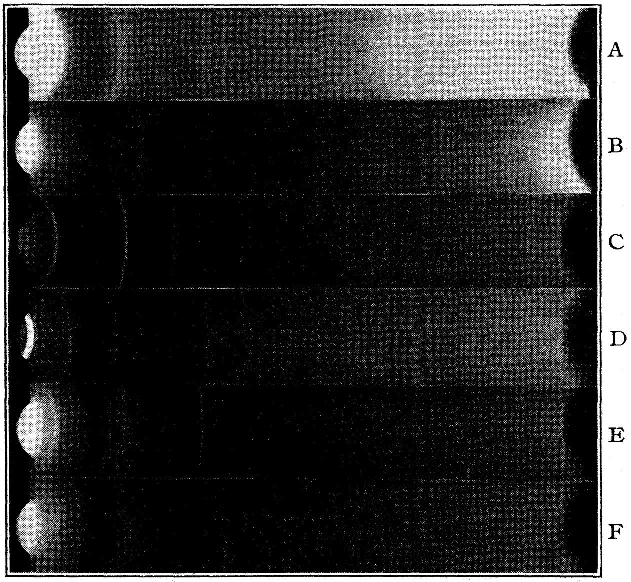

Fig. 1.—A, $Ni_2O_3{\cdot}2H_2O$ (A); B, NiO by decomp. of $Ni_2O_3{\cdot}2H_2O$ in air at 120°; C, $Ni(OH)_2$, obtained by decomposition of $Ni_2O_3{\cdot}2H_2O$ in water at 150°; D, preparation E_1 ($Ni_3O_4{\cdot}xH_2O$); E, preparation E_2 ($Ni_6O_7{\cdot}xH_2O$); F, preparation F ($Ni_2O_3{\cdot}H_2O$).

It was quite evident that removal of water alone above **a** content of two mols per Ni_2O_3 would not affect the x-ray diffraction, and that beyond this point the decomposition took place with loss in active oxygen. This strongly indicated that the original product was $Ni_2O_3{\cdot}2H_2O$, with some adsorbed water.

B. **A** solution of 20 g. of potassium hydroxide in 250 cc. of water was added dropwise to 50 g. of $Ni(NO_3)_2{\cdot}6H_2O$ in 250 cc. of water at 25°. **A** solution of 6 g. of potassium hydroxide and 6 cc. of bromine in 500 cc. water was then added to the suspended nickelous hydroxide. The reaction mixture was allowed to stand for five hours with intermittent stirring, before decantation was started. Purification was carried out as in **A.** The product was dried in an oil-pump vacuum over calcium chloride for three days. The x-ray diagram of the product was identical with that of product A (see Table I, 2). The Ni/O ratio in this case was 1/1.38, compared with the theoretical value of 1/1.5 for a hydrate of Ni_2O_3.

TABLE I

X-RAY DIFFRACTION DATA

1. **Preparations A, C and D Dried in *vacuo***

l in mm.	Intensity	Compd.
18	m, br	$Ni_2O_3·2H_2O$
24	s, br	$Ni_2O_3·2H_2O$
31	s, br	$Ni_2O_3·2H_2O$
39	vs, br	$Ni_2O_3·2H_2O$
68	m	$Ni_2O_3·2H_2O$
74	m	$Ni_2O_3·2H_2O$
121	m	$Ni_2O_3·2H_2O$
132	m	$Ni_2O_3·2H_2O$
143	vw	$Ni_2O_3·2H_2O$
155	vw	$Ni_2O_3·2H_2O$

2. **Preparation B Dried *in vacuo***

l in mm.	Intensity	Compound
25	s, br	$Ni_2O_3·2H_2O$
31	s, br	$Ni_2O_3·2H_2O$
39	vs, br	$Ni_2O_3·2H_2O$
68	m	$Ni_2O_3·2H_2O$
74	m	$Ni_2O_3·2H_2O$
122	m	$Ni_2O_3·2H_2O$
133	m	$Ni_2O_3·2H_2O$

3. **Preparation A Heated in Water at 150°**

l in mm.	Intensity	Compd.
39.0	vs	$Ni(OH)_2$
66.6	ms	$Ni(OH)_2$
72	vvw	NiO
77.4	vs	$Ni(OH)_2$
87	vw	NiO
104.3	ms	$Ni(OH)_2$
118.2	ms	$Ni(OH)_2$
125.3	mw	$Ni(OH)_2$
127	vw	NiO
138.8	vw	$Ni(OH)_2$
140.7	mw	$Ni(OH)_2$
145.4	mw	$Ni(OH)_2$
165.1	mw	$Ni(OH)_2$

4. **Preparation A Dried in Air at 130°C.**

l in mm.	Intensity	Compd.
73	m	NiO
86	s	NiO
125	s	NiO
149	mw, br	NiO
157	mw, br	NiO
219	mw, br	NiO

5. **Preparation C Dried in Air at 110° C.**

l in mm.	Intensity	Compd.
37	s	$Ni_2O_3·2H_2O$
68	wm	$Ni_2O_3·2H_2O$
74	s	$Ni_2O_3·2H_2O$, and NiO
85	s, br	NiO
121	mw	$Ni_2O_3·2H_2O$
123	m	NiO
132	mw	$Ni_2O_3·2H_2O$

6. **Preparation E_1 Dried *in vacuo***

l in mm.	Intensity	Compd.
21.2	s	$Ni_3O_4·xH_2O$
23.0	vs	$Ni_3O_4·xH_2O$
45.1	s	$Ni_3O_4·xH_2O$
67.8	m	$Ni_3O_4·xH_2O$
69.2	m	$Ni_3O_4·xH_2O$
76.7	mw	$Ni_3O_4·xH_2O$
90.5	w	$Ni_3O_4·xH_2O$
120.2	ms	$Ni_3O_4·xH_2O$
122.7	ms	$Ni_3O_4·xH_2O$
129.8	mw	$Ni_3O_4·xH_2O$
141.6	w	$Ni_3O_4·xH_2O$
200	vw	$Ni_3O_4·xH_2O$
242	vw	$Ni_3O_4·xH_2O$

7. **Preparation E_2 Prepared from E_1 at 110°C.**

l in mm.	Intensity	Compd.
25.0	vs	$Ni_6O_7·xH_2O$
37.8	ms	$Ni_6O_7·xH_2O$
48.7	w	$Ni_6O_7·xH_2O$
66.9	s	$Ni_6O_7·xH_2O$
76.0	m	$Ni_6O_7·xH_2O$
118.5	s	$Ni_6O_7·xH_2O$
121.8	vw	$Ni_6O_7·xH_2O$
125.2	vw	$Ni_6O_7·xH_2O$
139.3	vw	$Ni_6O_7·xH_2O$
145	vw	$Ni_6O_7·xH_2O$
196	vw	$Ni_6O_7·xH_2O$
235	vw	$Ni_6O_7·xH_2O$

l = linear distance between corresponding lines on each side of film. The following abbreviations are used to indicate relative intensities: s, strong; m, medium; w, weak; v, very; br, broad. The substances to which the various reflections were assigned appear in the columns headed "compd."

It was evident that oxidation of the suspended $Ni(OH)_2$ took place quite slowly, as another preparation with only a half-hour oxidation period resulted in a product of incomplete oxidation and showed only the diffraction of $Ni(OH)_2$. Precipitation and oxidation of $Ni(OH)_2$ at 100° produced a partially oxidized mixture showing the strongest diffraction lines of product A and $Ni(OH)_2$. Longer oxidation periods would doubtless have resulted in complete oxidation. The ultimate oxidation product was the same as by the method **A,** which was quite clearly revealed by the x-ray diffraction data.

C and D. These preparations were identical with **A,** except that the nitrate solutions were kept at 50 and 75°, respectively, during precipitation The products were dried in *vacuo* for three days. The x-ray diffraction patterns in both cases were identical with **A.** The only effect of higher temperatures of precipitation was to cause incomplete oxidation. If the unoxidized portion of product C was assumed to be $Ni(OH)_2$ the composition of the product was expressible as $0.25Ni(OH)_2 \cdot Ni_2O_3 \cdot 1.91H_2O$. With such a relatively small amount of $Ni(OH)_2$ present (ca. 10%) no diffraction effects of this compound were observed.

The product C was heated in air (water vapor pressure ca. 10 mm.) at 110° for periods of two, five and twenty hours. x-Ray diffraction patterns of the products (see Table I, 5) showed lines corresponding to the diffraction of NiO, increasing in intensity as the time of heating was increased The original pattern became much weaker. Analysis of the residue after twenty hours showed the material to contain 45.5% NiO, 40.5% Ni_2O_3, 13% H_2O and 0.5% CO_2. The $Ni_2O_3 : H_2O$ ratio was 1 : 2.9, somewhat higher than would be expected if the initial product was assumed to be $Ni_2O_3 \cdot 2H_2O$. However, about 10% of $Ni(OH)_2$ was evidently present in the initial product C, and as this would not lose water at the temperature of heating,[18] some of the water in the heated product must have been bound to divalent nickel (calculated as NiO).

The products **A,** B and C decomposed to $Ni(OH)_2$ when heated in Pyrex bomb tubes with water at temperatures of 130 to 150° for sufficiently long periods of time (several days). The end-products after three days heating at 150° showed very well defined diffraction patterns of $Ni(OH)_2$. (See Table I, 3, and Fig. 1C.) A few of the strongest diffraction lines of NiO appeared with very weak intensity. This might be expected since the material in the center of the particles would be in poor contact with water and tend to decompose as in the dry way. A portion of product **A** was partially decomposed in water at 128°, over a period of twelve hours. The analysis of the product was 34.0% NiO, 48% Ni_2O_3, 17.1% H_2O and 0.8% CO_2 showing the $Ni_2O_3 : H_2O$ ratio to be 1 : 1.7 on the assumption that all the divalent nickel was present as $Ni(OH)_2$. Since a small percentage of NiO always formed in such decompositions, this assumption was not strictly correct. Hence the $Ni_2O_3 : H_2O$ ratio would fall closer to 1 : 2, if all the water bound to trivalent nickel was taken into account. Such a value would be in agreement with decomposition according to the equation

$$Ni_2O_3 \cdot 2H_2O \longrightarrow 2Ni(OH)_2 + O$$

E_1. This preparation was identical with **A,** except that the nitrate solution was kept at 100° during precipitation. The product was purified in the usual manner, and dried *in vacuo* over calcium chloride for three days. The product was quite incompletely oxidized, the composition being 62.3% Ni_2O_3, 17.8% NiO, 19.9% H_2O, 0.5% CO_2 or $Ni_3O_{4.14} \cdot 3.34\ H_2O$. The x-ray diagram of the product was completely different from that of product **A** (see Table I, 6, and Fig. 1D). No lines of $Ni(OH)_2$ were visible. The product E_1 decomposed almost completely to $Ni(OH)_2$ when heated in water for three days at 150°. The end-product showed a very clear diffraction pattern of $Ni(OH)_2$, and very weak NiO lines (see Table II, 1).

E_2. Product E_1 was heated for four hours at 110° in air. The x-ray diagram of

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[18] Hüttig and Peter, *Z. anorg. allgem. Chem.*, 189, 183 (1930).

the product was completely different from that of A or E_1 (see Table I, 7, and Fig. 1E). No lines of NiO or $Ni(OH)_2$ were visible. The composition of the product was 31.4% Ni_2O_3, 51.7% NiO, 16.3% H_2O, 0.4% CO_2 or $Ni_6O_{7.06}\cdot 5.01H_2O$. Further heating at 110° for twenty hours caused no further change in the diffraction pattern. The product was heated for one day at 140° in air. The end-product gave a diffraction pattern showing the principal lines of NiO and a weakened pattern of the original product E_2. Product E_2 also decomposed to $Ni(OH)_2$ when heated in water at 150° for three days (see Table II, 2). The pattern of the end-product was identical with that of the end-product of the water-decomposition of E_1.

TABLE II

1. **Preparation E_1 Heated in Water at 150°**

l in mm.	Intensity	Compd.
38.6	vs	$Ni(OH)_2$
66.9	s	$Ni(OH)_2$
72	w	NiO
76.9	vs	$Ni(OH)_2$
87	mw	NiO
103.8	ms	$Ni(OH)_2$
117.5	ms	$Ni(OH)_2$
124.8	ms	$Ni(OH)_2$
138.2	w	$Ni(OH)_2$
140.2	m	$Ni(OH)_2$
144.9	m	$Ni(OH)_2$
164.3	m	$Ni(OH)_2$

2. **Preparation E_2 Heated in Water at 150°**

l in mm.	Intensity	Compd.
39.2	vs	$Ni(OH)_2$
66.5	ms	$Ni(OH)_2$
73	mw	NiO
77.6	vs	$Ni(OH)_2$
88	ms	NiO
104.5	ms	$Ni(OH)_2$
118.1	m	$Ni(OH)_2$
125.2	m	$Ni(OH)_2$
127.3	mw	NiO
138.3	w	$Ni(OH)_2$
141.1	m	$Ni(OH)_2$
145.4	m	$Ni(OH)_2$
165.1	mw	$Ni(OH)_2$

3. **Preparation F Dried in vacuo**

l in mm	Intensity	Compd.
25.7	vs	$Ni_2O_3\cdot H_2O$
51.5	s	$Ni_2O_3\cdot H_2O$
68	vw, br	$Ni_2O_3\cdot H_2O$
73.5	m	$Ni_2O_3\cdot H_2O$
76	mw, br	$Ni_2O_3\cdot H_2O$
85	vw	$Ni_2O_3\cdot H_2O$
122	vw, br	$Ni_2O_3\cdot H_2O$
131.5	m	$Ni_2O_3\cdot H_2O$
134.7	mw	$Ni_2O_3\cdot H_2O$
144	vw	$Ni_2O_3\cdot H_2O$
156	vw	$Ni_2O_3\cdot H_2O$
225	vw	$Ni_2O_3\cdot H_2O$

4. **Preparation F Heated in Air at 120°**

l in mm.	Intensity	Compd.
25	s, br	$Ni_2O_3\cdot H_2O$
51	w, br	$Ni_2O_3\cdot H_2O$
69	vw, br	$Ni_2O_3\cdot H_2O$
74	ms, br	$Ni_2O_3\cdot H_2O$ and NiO
87	m, br	NiO
124	mw, br	NiO
132	m, br	$Ni_2O_3\cdot H_2O$

Preparation F Heated in Water (Steel Bomb) at 150°

l in mm.	Intensity	Compd.
39.2	w	$Ni(OH)_2$
66.6	vvw	$Ni(OH)_2$
73[illegible]	s	NiO
77.5	w	$Ni(OH)_2$
87	vs	NiO
104.5	vw	$Ni(OH)_2$
118.4	vvw	$Ni(OH)_2$
124	s	NiO
141	vvw	$Ni(OH)_2$
145	vvw	$Ni(OH)_2$
150	m	NiO

F. Since it appeared that E_1 was a compound containing both di- and trivalent nickel, and not a mixture of compounds, it was important to know the effects of further oxidation. E_1 was prepared as described above. After precipitation the suspended product was divided into two equal portions. One was purified and dried in air. The x-ray diffraction of this product was identical with that of E_1, and the composition of the product was 54.1% Ni_2O_3, 19.8% NiO, 23.8% H_2O, 1 9% CO_2 or $Ni_3O_{4.07}$ $4.31H_2O$. The other half of the precipitate was further oxidized at 25° by addition of a solution containing 20 g. of potassium hydroxide and 5 cc. of bromine in 250 cc. of water. The product was allowed to stand for an hour and then decanted ten times, filtered, washed and dried in *vacuo*. It was quite noticeable that this precipitate settled more rapidly than the previous preparations. In most cases peptization occurred on the third decantation, and a large percentage of the product was lost during decantation. In this preparation peptization did not occur to any great extent until the eighth decantation, indicating that the excess base was more strongly adsorbed by the product than in the previous cases. The x-ray diffraction pattern of this product, F, was entirely different from any of the foregoing (see Table II, 3, and Fig. 1F). The product had the composition $Ni_2O_{3\ 10}\cdot 1.57H_2O$. The product was heated for ten hours at 110°. The partially decomposed product contained 77.6% Ni_2O_3, 12.3% NiO, 8.5% H_2O and the $Ni_2O_3 : H_2O$ ratio of the undecomposed material was 1 : 1.01. Faint indications of NiO lines appeared on the diffraction diagram of the heated product, along with the weakened lines of the original pattern. Further heating at 120° for five hours produced a mixture the diffraction pattern of which clearly showed the principal lines of NiO (see Table II, 4). These results indicated that the product F was essentially the monohydrate of Ni_2O_3, and decomposed according to the equation

$$2(Ni_2O_3 \cdot H_2O) \longrightarrow 4NiO + 2H_2O + O_2$$

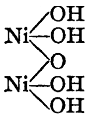
The product F was heated at 150° for three days in a Pyrex bomb tube. The x-ray diagram of the product showed NiO lines and also some new lines which must have been caused by the presence of a nickel silicate, since analysis showed that the end-product contained about 20% of silica The decomposition in water was repeated in a steel bomb, and the product gave strong diffractionlines of NiO along with very weak $Ni(OH)_2$ lines. Comparison with the diffraction pattern of a known mixture of 20% $Ni(OH)_2$ and 80% NiO formed by decomposition of $Ni_2O_3 \cdot 2H_2O$ at 160° in air showed that the amount of $Ni(OH)_2$ present in the end-product was less than 20%. Thus it appeared that the primary decomposition product of $Ni_2O_3 \cdot H_2O$ in both air and water was NiO. The small amount of $Ni(OH)_2$ that formed during the decomposition in water was apparently due to impurities in the original product F.

Discussion

Due to their fine state of subdivision the compounds prepared in this work contained quite variable amounts of water. However, the analyses of the partially decomposed products, obtained by heating in air, coupled with the results of the x-ray diffraction experiments, were successful in establishing for the first time the existence of compounds having the compositions $Ni_2O_3 \cdot 2H_2O$ and $Ni_2O_3 \cdot H_2O$. Although such compounds have been previously termed "hydrates," there is considerable evidence to indicate that they do not possess the properties of true hydrates. Since the compound $Ni_2O_3 \cdot H_2O$ was prepared in water at a temperature at which $Ni_2O_3 \cdot 2H_2O$ was stable, and since there was no indication of formation of the latter compound after the monohydrate had stood in water for two weeks during the purification process, it was evident that the transition $Ni_2O_3 \cdot H_2O + H20 \longrightarrow Ni_2O_3 \cdot 2H_2O$ did not take place. Furthermore, the reverse change did not take place when the dihydrate was decomposed by heat, but instead a complete decomposition took place

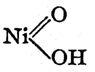
$$2(Ni_2O_3 \cdot 2H_2O) \longrightarrow 4NiO + 4H_2O + O_2$$

The fact that the dihydrate could be prepared by oxidation of $Ni(OH)_2$, and decomposed to that compound on heating in water, was not consistent with the assumption that the compound was a true hydrate. It has been impossible to prepare Ni_2O_3 by dehydration of such compounds, since the loss in water is always accompanied by a loss in active oxygen. There is no reason to believe that the removal of water of crystallization would affect the oxygen linkage. On the other hand, the assumption that the compounds $Ni_2O_3 \cdot 2H_2O$ and $Ni_2O_3 \cdot H_2O$ have the following structures was in complete accord with the experimental observation



I

or $Ni_2O_3 \cdot 2H_2O$



II

or $^1/_2$ $Ni_2O_3 \cdot H_2O$

The decomposition of product F into NiO in water and air alike was strongly indicative of a structure of type II. It was previously shown[17] that the transition $NiO + H_2O \longrightarrow Ni(OH)_2$ would not take place under the conditions of the above experiments, and that $Ni(OH)_2$ was stable in water at the temperatures employed.[18] Hence any NiO or $Ni(OH)_2$ formed in the above decompositions must have been primary decomposition products. It would be expected that $Ni(OH)_2$ could be formed directly from a compound of type I, but not from one of type II, and this expectation was borne out by the results of the decomposition of the mono- and dihydrates in water. Hence the above structures were satisfactory from this standpoint.

Hofmann and Hiendlmaier[19] reported a compound which had the composition $KNiO_2$, by fusion of nickel powder with potassium peroxide. This was possibly a salt of the compound II. Hydrolysis took place in water, and the hydrolyzed product gave the analysis $Ni_2O_3 \cdot 2H_2O$, but part of this water might well have been adsorbed. The acidic nature of the product F was indicated by its relatively slow rate of peptization, indicating a strong retention of base, as would be the case if a weak salt were formed.

It was apparent that the method of isobaric decomposition employed by Hüttig and Peter[1]* in establishing the existence of the monohydrate was not

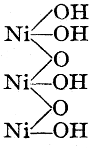
(19) Hofmann and Hiendlmaier, *Ber.*, 39, 3184 (1906).

conclusive, for the decomposition of the dihydrate has been shown to be irreversible. Their initial preparation consisted of the dihydrate, and in view of the present work it is improbable that they obtained the monohydrate by decomposition of this product. Furthermore, they found no evidence for the existence of the dihydrate, which they should have obtained had the method been reliable. Also the later work of LeBlanc and Müller[15] supports this conclusion very strongly.

The present results are not in accord with those of Hiittig and Peter in two other important respects. They found that no active oxygen was lost when a compound corresponding to the dihydrate was heated for several hours in water at temperatures of 120 and 200°. The product formed in the latter case was assumed to be the monohydrate of Ni_2O_3. In the present work it was found that the decomposition in water at 130 to 150° took place directly to nickelous hydroxide. The heating times were much longer than in the case of the previous work, but there was no evidence of intermediate compounds formed in the decomposition. Also the x-ray diagram of the "monohydrate" obtained by them in this way did not correspond to the pattern of that compound obtained in this work.

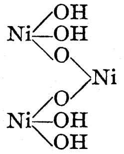
The identity of the diffraction patterns of products A and B left no doubt as to the fact that the oxidized product was the same in each case, *i. e.*, whether by simultaneous oxidation and precipitation, or by oxidation of previously precipitated nickelous hydroxide. Hiittig and Peter obtained differing diffraction patterns for preparations similar to the above, and this might have been due to incomplete oxidation of the nickelous hydroxide, since the oxidation of the suspended material was found to take place quite slowly.

Little could be said as to the exact nature of the preparations E_1 and E_2 other than that it was evident that they were compounds containing both di- and trivalent nickel and not mixtures of a trivalent oxide-hydrate and NiO or $Ni(OH)_2$. If E_1 had been such a mixture, further oxidation would only have oxidized the divalent compounds present and left the trivalent compound unchanged. Thus the properties of the product would have changed very little due to such an oxidation. However, the results were quite different from this. The oxidized product F not only gave a different diffraction pattern, but also behaved completely differently on decomposition in water and air. Hence the original product E_1 must have been completely changed by the oxidation, and this would only be the case if it were a compound of di- and trivalent nickel. The chemical analyses indicated that the compositions of E_1 and E_2 could be expressed as hydrates of the hypothetical oxides Ni_3O_4 and Ni_6O_7, but their properties indicated that the water was bound in the compounds as hydroxyl groups. The following were the simplest structures which could be devised



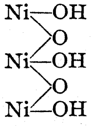
IIIa

or $Ni_3O_4 \cdot 2H_2O$
Mono nickelous (basic)
salt of I



IIIb

Mono nickelous salt of
ortho nickelic acid



IV

or $^1/_2Ni_6O_7 \cdot 3H_2O$
Di-nickelous (basic) salt of
ortho nickelic acid

It is obvious that such compounds might hydrolyze to nickelous hydroxide, as was observed when E_1 and E_2 were heated in water. The water contents of compounds of types III and IV are somewhat below the observed contents of E_1 and E_2, but this does not exclude the possibility that these are the correct structures, for considerable amounts of water are frequently adsorbed by such precipitates, as shown in the previous discussion. We favor formula IIIa over IIIb since IV may be obtained from it without rearrangement. (This transition takes place upon heating of compound III.)

Summary

1. The existence of compounds having the compositions $Ni_2O_3 \cdot H_2O$ and $Ni_2O_3 \cdot 2H_2O$ has been shown. Characteristic x-ray diffraction patterns of these compounds have been obtained.

2. The modes of decomposition of these "hydrates" in water and air at temperatures of 100 to 150° have been established with the aid of x-ray analysis. The results indicated that the compounds were not true hydrates, but contained the water bound as hydroxyl groups. Structural formulas have been assigned.

3. Two compounds of nickel, oxygen and water, at lower stages of oxidation than the above, have been isolated, and their diffraction patterns obtained. Chemical analyses indicated that they were hydrates of the hypothetical oxides Ni_3O_4 and Ni_6O_7, but their behavior on decomposition showed them to be of a type analogous to the above compounds. Reasonable structural formulas have been proposed.

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The Diffusion of Colloidal Electrolytes; Sodium Oleate

BY M. E. LAING MCBAIN

Soaps afford one whole family of uni-univalent electrolytes to which the hypothesis of complete dissociation is not reasonably applicable.[1] In very dilute solution they are only moderately strong electrolytes and in more concentrated solutions they are colloidal electrolytes. In such cases the high diffusion constant observed[2] is a composite made up from the various ionic molecular and colloidal species present. The accepted formulas of Nernst[3] and Haskell[4] refer, however, only to infinite dilution and that of Einstein[5] to uncharged spherical molecules or particles. McBain and Liu,[6] from a consideration of the principles of interionic attraction as analyzed in the Debye–Hückel–Onsager theory and from experimental data for potassium chloride, sucrose, and potassium laurate, derived four conclusions for dealing with ordinary finite concentrations: (1) that the resistance of ions to motion, all in the same direction, is nearly independent of their concentration; (2) that the change in diffusion coefficient of an electrolyte such as potassium chloride is dependent primarily upon a direct proportion to the observed osmotic pressure rather than to the numerical value of the activity;[7] (3) for non-electrolytes the diffusion coefficient is not greatly affected by the changes in viscosity with concentration and, therefore, usually diminishes but slowly with increase in concentration; (4) that the total diffusion observed may be arrived at in good first approximation by combining additively (a) the diffusion of known concentrations of molecules and of uncharged colloidal particles, using the Einstein equation, (b) the Nernst equation (for infinite dilution) for the ions of a uni-univalent electrolyte but corrected for decrease in osmotic pressure, and (c) the Haskell formula (for infinite dilution) corrected for change in osmotic pressure for polyvalent electrolytes or charged colloidal particles together with their compensating ions.

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(1) McBain, THIS JOURNAL, 50, 1636 (1928).

(2) (a) McBain and Liu, *ibid.*, **53**, 59 (1931): (b) see also Hartley and Robinson, Proc. *Roy Soc.*, (London), **A134**, 20 (1931); (c) Svedberg, *Kolloid-Z.*, **36**, Erganzungsbd., p. 63 (1925), equations 13b and 14.

(3) Nernst, *Z. physik* Chem., 2,613 (1888); "Theoretische Chemie," 10th ed., 1921, pp. 425–431.

(4) Haskell, *Phys.* Rev., [1] 27, 145 (1908).

(5) Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

(6) McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

(7) Compare G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1623, p. 362. The approximate proportionality to the observed osmotic pressure was experimentally demonstrated by Öholm [Z. *physik.* Chem., 60, 343 (1904)] over the whole range of concentrations of solutions of electrolytes up to several times molar. He showed the advisability of correcting for viscosity, but found a direct proportion an over correction; MacInnes much later proposed $\eta^{0.7}$. Hartley [*Phil* Mag., 12, 485 (1931)] used this and compared the replacement of van't Hoff's i by d In $a_{\pm}$/d In C for electrolytes in fairly dilute solution (0.1 N) with an average discrepancy of over 4%. For higher concentrations he writes "... an exact comparison would not, in the present state of the latter, be instructive, even if the method and assumptions of the theory could he considered applicable in the more concentrated solutions."

For the simple case of a highly dissociated uni-univalent electrolyte such as potassium chloride the diffusion coefficient D in sq. cm./day is

$$D = iRT\Big/\left(\frac{1}{U} + \frac{1}{V}\right)$$

where U and V are the mobilities in reciprocal ohms of cation and anion; that is, the denominator is the sum of the resistances to movement and the numerator is the driving force, i being the van't Hoff osmotic coefficient.

Their general equation for such an electrolyte, partially dissociated[8] (or ions, partially "associated), α referring to concentrations, is

$$D = \frac{i}{1 + (n - 1)\alpha} RT \left[\alpha \left(\frac{1}{n_+} + \frac{1}{n_-}\right) \left(\frac{1}{\frac{1}{U} + \frac{1}{V}}\right) + \frac{1 - \alpha}{1/U_m}\right]$$

where n is the number of ions produced by the dissociation of one molecule or particle, n_+ and n– are the valencies of cation and anion, $1/U$ and $1/N$ are the resistance to movement of one electrochemical equivalent (charge of IF) in each case, whereas $1/U_m$ is the resistance to movement of *1* whole gram molecule (or 60.6 X 10^{22} "uncharged particles") as defined in the Einstein equation.

$$D = \frac{RT}{N6\pi\eta r} = \frac{RT}{1/U_m}$$

RT has the value[9] of 0.02246 at 18° and 0.02300 at 25° if $1/U_m$ is expressed in ohms. The formula is for diffusion into pure solvent. For diffusion into another solution, slightly less concentrated, the gradient of osmotic pressure with concentration would be used.

It follows directly from these equations that if a large particle or a molecule of low mobility such as a protein passes from the isoelectric point to become a polyvalent electrolyte, its diffusion is accelerated almost in proportion to the total number of ions of the polyvalent electrolyte. This was first derived implicitly in 1925 by Svedberg,[2c] who suggested that diffusion might thus be used for measuring how many charges are carried by a single particle.

It is interesting that the diffusion constant of mercuric chloride, 0.92, which admittedly consists almost entirely of molecules, is very nearly that

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(8) Owing to the circumstance that in the special case of potassium chloride $1/U_m = 1/U + 1/V$, McBain and Liu wrote this in the equivalent form, not generally applicable

$$D = \frac{iRT}{\alpha\frac{1}{U} + \alpha\frac{1}{V} + (1 - \alpha)\frac{1}{U_{\text{KCl}}}}$$

They committed the algebraic error of recording D as $iRT/$(sum of resistances), instead of, as in their actual numerical examples, keeping the added fractions separate, the numerators adding to iRT. G. S. Hartley's suggested emendation is obviously erroneous as may be seen if it is considered in connection with a weak electrolyte such as mercuric chloride or succinic acid. He multiplies the diffusion of the neutral molecule by the valencies of the ions into which it would have dissociated had it been dissociated [*Phil.* Mag., 12, 487 (1931)]. He states at the top of p. 487 that McBain and Liu ignored interionic forces, having overlooked their discussion.

(9) Values calculated from data of "International Critical Tables."

calculated for complete dissociation into independent ions, 0.91. The resistance to movement of the molecule is, therefore, one-third the sum of the three ions. For cadmium iodide, a stronger electrolyte, the diffusion coefficient for completely undissociated molecules is 0.67 as compared with 1.18 for complete dissociation, the resistance for the molecule being 58% of the sum of that of the three ions. From these and other data one might tentatively infer that the more polar the molecule the less differences does dissociation cause in resistance to movement and hence, conversely, the greater the importance of the mere number of molecules and ions present.

The present paper supplements the above analysis of the diffusion of potassium laurate[2a] with more extended data for sodium oleate. Here it is possible to test the effect of the linking of the primary particles of oleate by showing that diffusion from sodium oleate jelly into water is just as rapid as the diffusion of the oleate sol.

Experimental

The method employed was that previously described,[2a] in which a Northrop diffusion cell is filled with the soap solution which diffuses through a sintered Jena glass membrane into 0.0015 N sodium hydroxide to prevent hydrolysis. As in previous experiments the same values are obtained with each of the four cells used, lower values being found only with a very tight, slow diffusing membrane when studying the higher concentrations of soap. However, the values for dilute solutions, using the same slow cell, lie on the general curve, and it is supposed then that these finer pores became clogged in higher concentrations, either with soap or with fatty acid formed by hydrolysis. Additional tests with cells at 20 and 25° have been carried out and have checked the previous assumptions that different cells yield the same diffusion constants.

The properties of the cells used are given in Table I. The sintered glass membrane was in every case 5 cm. in diameter and 2 mm. thick.

TABLE I

CHARACTERISTICS OF THE DIFFUSION CELLS

Designation		Volume of cell, cc.	Approx. pore radius, Å.	Cell constant
Trade	Here			
G-4	a	37.08	2.5×10^4	348.2
G-4	b	37.96	2.5×10^4	170.2
G-3	G-3	98.00	$(15–20) \times 10^4$	348.3
G-4	W	106.9	2.5×10^4	253.0
G-4	M	105.3	2.5×10^4	221.8

The diffusion method is accurate to a fifth of one per cent. for electrolytes, but for soaps the error may be increased to several per cent. owing to the extreme difficulty of releasing the air from the soap solutions. Early attempts to find the boiling point of soap solutions[10] failed completely

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(10) Compare McBain and Taylor, *Z. physik. Chem.*, **76, 179 (1911)**.

because of the air obstinately retained. In many of the diffusion experiments recorded here, however, only a few bubbles were developed if the solutions had previously been thoroughly subjected to suction. The experimental results are calculated by the formula developed by Liu, and displayed in Fig. **1,** where data for sucrose and potassium laurate are added for comparison. New values added for **0.05** N_w potassium laurate are D = **0.510** and **0.510.**

TABLE II

DIFFUSION OF ORDINARY ISOTROPIC SOLUTIONS OF SODIUM OLEATE AT 25°

Concn. N_w	Cell	Time in hours	Concn. change in g. equivalents	D
0			(Predicted)	0.731
0.0250	[a]	56.00	0.001668	.461
.0250	W	23.33	.000798	.463
.0253	(b)	90.00	.001883	.496
.0456	(a)	47.65	.003138	.388
	G-3	47.42	.003088	.387
	(a)	47.66	.003170	.392
.0490	G-3	48.00	.003212	.365
.0503	G-3	17.74	.001282	(.368)[b]
.098	M	40.81	.003303	.322
	W	40.85	.003753	.322
.150[c]	(a)	41.00	.006260	.265
	(a)	24.33	.004027	.281
	G-3	22.00	.003567	.280
.300	(a)	19.00	.004922	.217
	G-3	17.50	.004458	.215
	(a)	17.63	,004856	(.233)
.376	W	22.00	.005320	.214
	G-3	22.00	.006905	.214
.500	G-3	26.00	.01172	.229
	G-3	23.75	.01235	.224

[a] Mean of cells M and W. [b] From residue (0.328). from diffusate (0.407). [c] At 20°.

Discussion of Results

We may compare the observed results (a) with the predictions of the Nernst and Haskell equations and (b) with values for other substances (see Fig. 1). Taking the mobilities of potassium and sodium from the data of "International Critical Tables" and that of a simple fatty ion as **23.2** and assuming the equivalent conductivity of the ionic micelle to be equal to that of the potassium ions, we calculate from the Nernst equation for complete dissociation into simple ions D = **0.813** for potassium laurate and D = **0.731** for sodium oleate. Again the Haskell formula for hypothetical complete dissociation into a decavalent ionic micelle and **10** alkali ions yields D = **0.936** for the ionic micelle (plus potassium ions) of potassium laurate and D = **0.759** for that of sodium oleate. It is noteworthy that these numbers show a distinctly higher rate of diffusion for the colloid form as compared with the simple ions, assuming infinite dilution in both cases.

However, for colloidal soap this is offset by the much lower diffusion velocity of the undissociated colloid or neutral micelle which is present in even larger quantity than this ionic micelle and for which the driving force per colloid particle is only one-eleventh that on the ionic micelle with its ten compensating ions. Thus in Fig. **1** the observed diffusion values are much lower than those calculated above because of the incomplete dissociation both of the simple molecules in dilute solution and of the colloidal electrolyte in more concentrated solution. Once the colloidal electrolyte is fully formed, as in **0.3** N solution upward, its diffusion, like its apparent degree of dissociation, changes very little with concentration.[11] As a matter of fact, the observed diffusion rate is an approximately linear function of the proportion of total colloid.

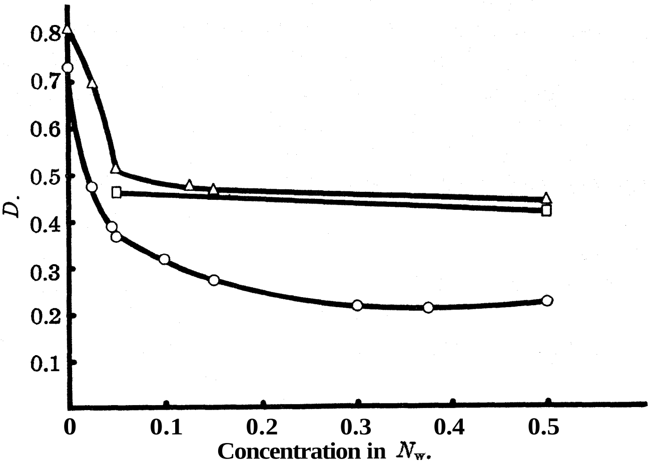

Fig. 1.—The diffusion coefficients D in sq. cm./day of potassium laurate, sucrose, and sodium oleate, at 25°; A, potassium laurate; □, sucrose; O, sodium oleate.

A 0.025 N_w sodium oleate solution contains only 1.5% of colloid, accounting for **0.011** of the observed diffusion, **0.462,** leaving 0.451 for simple ions and molecules. The composition diagram of these solutions was published by McBain, Laing and Titley,[12] but the Arrhenius conductivity ratio was not then corrected for interionic attraction, so that the *25%* Arrhenius dissociation (left after allowing for products of hydrolysis) really means about 26.3% true dissociation. This correction, however, is partly offset by the lowering of osmotic pressure. 26% of **0.731** is 0.190 which

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[11] This is a further confirmation of the point made by McBain that for the ionic micellrs of soap the charges are so widely spaced that the ionic strength of the solution is only that of a uni-univalent salt [THIS JOURNAL, 50, 1636 (1928)].

[12] McBain, Laing and Titley, *Trans. Chem. Soc.*, 115, 1279 (1919).

when subtracted from 0.451 leaves 0.268 due to the diffusion of simple molecules which comprised 61% of the total soap. Their diffusion constant $D_m = 0.261/0.61 = 0.428$, and their mobility from the Einstein formula 18.6. This is somewhat less than the mobility of the oleate ion (23.2), and the resistance to movement of this more strongly polar molecule is 85% of the sum of its two ions in accordance with the tentative rule on a previous page.

In 0.5 N solution of sodium oleate the only constituents present are ionic micelle and its sodium ions and the neutral colloid. The Arrhenius conductivity ratio was 20%, which as a first approximation may be corrected by comparing it with the Arrhenius ratios for decinormal solutions,[13] thus indicating a true degree of dissociation of about 23.5%. This again from the standpoint of diffusion is partly offset by the lowering of osmotic pressure due to interionic attraction.[14] Approximately, then, the diffusion due to the ionic micelle and its ions may be taken as 22% of 0.759 (see above) = 0.167. This subtracted from the observed value of 0.226 leaves 0.059 for the 76.5% of neutral micelle, whose diffusion coefficient is, therefore, 0.077 and mobility U_m is 3.35. From this, Einstein's equation for a spherical uncharged particle would give a diameter of only 55 Å.

The size of the primary particle of neutral colloid is, therefore, only a little greater for sodium oleate than for potassium laurate[2a] (48 Å.). In both cases the ionic micelle, from the mobility assumed, has an effective diameter of 25 Å. The small size of the primary particles of soap solutions is confirmed by measurements on light scattering to be reported elsewhere. It thus appears that the great difference experimentally observed between potassium laurate and sodium oleate is not essentially due to difference in size of the primary particles but to the fact that in the sodium oleate there is a great tendency for the formation of loose secondary aggregates. The light scattering does not change when sodium oleate sol sets to a clear jelly.[15] Potassium laurate, on the contrary, does not show the slightest tendency to gelatinize even in the presence of salts; and it passes through fine ultrafilters.

Diffusion of Sodium Oleate Jelly.—Having found that the relatively high viscosity and ready ultrafilterability must be ascribed to loose aggregation of the neutral colloidal particles, it becomes of great interest to note that this has interfered to only a very minor extent with the diffusion coefficient of the sol. This may be pictured as a comparison between the diffusibility of a number of particles loosely strung together, as in a flexible necklace, with their diffusibility when completely separated. McBain and Liu[2a] pointed out the remarkable fact that with sucrose a manifold increase of viscosity caused by diffusing molecules themselves only slightly

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(13) Compare Kraus, "Properties of Electrically Conducting Systems," 1922, p. 35, Table 4

(14) Ref. 13, pp. 233, 234.

(15) McBain and McBain, *Nature*, 126, 125 (1930).

affects the rate of their diffusion. Upon the same principle, the necklace would be expected to diffuse almost *as* fast as the component beads.[16]

The following experiments were carried out to ascertain how fast sodium oleate diffuses from the completely jellied form into water (with **0.0015** N sodium hydroxide). Comparative experiments were likewise made with other portions of the same specimen of solution which had been allowed to crystallize out far enough to form a hard white curd and with two intermediate samples in which only a small amount of curd fibers had separated.

TABLE III

DIFFUSION FROM DIFFERENT SAMPLES OF THE SAME 0.5 N_w SODIUM OLEATE SOLUTION IN DIFFERENT PHYSICAL STATES

State of soap	Temp., °C.	D in sq. cm./day	
Clear sol	25	0.221	0.221
Clear jelly	25	.232	.228
Cloudy gel	25	.186	.194
Translucent cloudy gel	23–25	.187	.189
Hard white curd	22–23	.135	.149

It is really quite remarkable to find that soap can diffuse as fast when its colloidal particles are fixed as when they are fluid and free to move and that the diffusing power is only lessened when the amount of material present decreases by crystallizing out as it does in curding, which removes soap from solution. This finding would exclude loose aggregation as a noticeable cause of lessened diffusibility of colloids.

Summary

1. General equations for diffusion are given to comply with the experimental fact that diffusion is proportional to osmotic pressure and not to activity.

2. It is suggested that the resistance to movement of an undissociated molecule is dependent upon its degree of polarity.

3. Colloidal electrolytes such as soaps exhibit high diffusion coefficients, which are analyzed. Primary particles of sodium oleate are not much larger than those of potassium laurate. The viscosity and gelatinizing power of sodium oleate is due to loose linking of primary particles and this does not appreciably affect the rate of diffusion.

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(16) Svedberg and Chirnoaga [THIS JOURNAL, 50, 1399 (1928)] have adopted an exactly opposite point of view to explain the discrepancy observed with hemocyanin between diffusion and sedimentation velocity which, however, must become identical for sedimentation equilibrium at all concentrations.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 325]

The Free Energy of Formation of Iodine Monobromide in Carbon Tetrachloride Solution

BY DON M. YOST, THOMAS F. ANDERSON AND FOLKE SKOOG

Introduction

Inasmuch as the extent of dissociation of gaseous iodine monobromide into gaseous iodine and bromine is known,[1] it was considered of interest to determine the corresponding dissociation when all substances are present in a nearly ideal solvent, such as carbon tetrachloride. From such data the corresponding dissociation in aqueous solution can also be obtained when distribution experiments are made.

In this paper are presented the results of measurements on the vapor pressures of iodine monobromide above its carbon tetrachloride solutions, together with the thermodynamic quantities calculated by combining the results with other known data.

Experimental Method and Preparation of the Materials

The vapor pressure of iodine monobromide above its solutions in carbon tetrachloride was measured by passing dry nitrogen at constant pressure at the rate of about one liter per hour through a series of bulbs containing the monobromide solution at 25.0". All-glass connections were used throughout. The total amount of halogens removed by the nitrogen was small compared with the amounts present in the solutions, and hence the concentrations were not appreciably changed.

It was necessary in all experiments to analyze for both the total halogen and the iodine in order to establish the composition of the vapor. This was accomplished by the analyses of two separate samples. In one sample the halogens were absorbed in potassium iodide solution and the liberated iodine titrated with standard thiosulfate. this procedure serving for the determination of the total halogen. In a second sample the halogens were absorbed by an excess of sodium sulfite solution, 0.5 N hydrochloric acid was added, and the iodide present was titrated with standard permanganate, the end-point being determined electrometrically.[2] In this latter determination a sudden increase in the e. m. f. takes place when all of the sulfite has been oxidized, and a second increase is observed when all of the iodide has been converted to iodine. For the oxidation of all but a trace of the sulfite a more concentrated permanganate solution was used. It was found that this procedure could be used for quantities of iodine as small as 0.1 milliequivalent with an accuracy of 1.0%, the accuracy increasing with an increase in the amount determined.

The iodine used was a product of high quality, the purity of 99.97% indicated by the manufacturer having been confirmed in this Laboratory. Bromine marked c. p. was twice distilled from very pure potassium bromide and then from phosphorus pentoxide, and the middle fraction from the last distillation was used in the experiments. The resulting material was sealed in glass tubes of known weight and the tubes with their contents weighed. The solutions of iodine monobromide were prepared by dissolving

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(1) McMorris and Yost, THIS JOURNAL, 53, 2625 (1931).

(2) Gorbatscheff and Kassatkina, *Z. anorg. allgem. Chem.*, 191, 104 (1930); Hahn, *ibid.*, 190, 75 (1930-1931).

exactly equivalent amounts of iodine and bromine in measured volumes of carbon tetrachloride.

To obtain pure carbon tetrachloride the C. P. material was saturated with chlorine and the chlorine removed by boiling. The residue was then redistilled and the middle fraction collected and used in the experiments.

Results of Experiments

In Table I are presented the results of the experiments made to determine the partial pressures of iodine monobromide over solutions of it in carbon tetrachloride. Each pressure is the average for several determinations in which the average deviation from the mean was 2%.

TABLE I

PARTIAL PRESSURES OF IODINE MONOBROMIDE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS

Mole fraction $IBr + I_2 + Br_2$	Pressure $IBr + 2I_2$	Pressure $IBr + Br_2 + I_2$	Mole fraction N of IBr	Pressure p of IBr	Ratio $k = p/N$
0.00179	0.202 mm.	0.229 mm.	0.00165	0.198 mm.	120[a]
.00390	.413	.476	.00355	.405	114
.00805	.860	.990	.00735	.842	115
.0108	1.17	1.32	.0100	1.15	115
.0224	2.36	2.68	.0207	2.32	112
				Mean	114

[a] This value was not included in estimating the mean.

That Henry's law, p/N = constant, is obeyed over a considerable range of concentration, is evident from the values of the constant given in the last column of the table.

In all experiments the vapor contained an excess of bromine, this excess being due to the presence in the solutions of free bromine, which results from the dissociation of the iodine monobromide. Under the assumption that the free bromine in the vapor is, to a first approximation, equal to the excess found, and by using for the Henry's law constant p_{Br}/N_{Br} for bromine in carbon tetrachloride solution the value[3] 409, expressed in millimeters, an approximate value for the mole fraction of free bromine in solution was calculated. Since iodine and bromine were present in equivalent amounts in solution the mole fraction of free iodine was equal to that of the bromine. The partial pressure of iodine, calculated by employing the value[4] 26.9 for the constant of Henry's law, was used to correct the partial pressure of free bromine. A second approximation was found unnecessary.

It is also possible to estimate the composition of the vapor by applying the known value for the dissociation constant of iodine monobromide to the results of the analyses. The two methods of calculation lead to the same result within the limits of experimental errors. The method used

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(3) Lewis and Storch, THIS JOURNAL, 39, 2544 (1917).

(4) This value was calculated from known values for the solubility of iodine in carbon tetrachloride and the vapor pressure of the solid at 25.0°. Jakowkin, *Z. physik. Chem.*, 18, 588 (1885); Baxter Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

above makes possible an independent evaluation of the extent of dissociation of the monobromide both in solution and in the gaseous state, and it was for this reason that it was chosen. It must be noted, however, that small differences between large quantities are involved and consequently the dissociations so calculated are subject to much greater errors than those given below.

The free energy changes accompanying the following changes in state were obtained directly from the literatures or by an application of the relation

$$\Delta F^\circ_{298} = -RT\ln K$$

to the known values K, of vapor pressures, solubilities and constants of Henry's law. The Henry's law constant p/N for the iodine monobromide is 114/760, the numerator being the mean value given in Table I.

$$\begin{aligned}
&\tfrac{1}{2}I_2\,(s) + \tfrac{1}{2}Br_2\,(l) = IBr\,(g) && \Delta F^\circ_{298} = 903\text{ cal.}^{1} && (1)\\
&\tfrac{1}{2}I_2\,(\text{in } CCl_4) = \tfrac{1}{2}I_2\,(s) && \Delta F^\circ_{298} = -1330\text{ cal.}^{6} && (2)\\
&\tfrac{1}{2}Br_2\,(\text{in } CCl_4) = \tfrac{1}{2}Br_2\,(l) && AF = -195\text{ cal.}^{5} && (3)\\
&IBr\,(g) = IBr\,(\text{in } CCl_4) && \Delta F^\circ_{298} = -1124\text{ cal.} && (4)\\
&\text{Hence, } \tfrac{1}{2}I_2\,(\text{in } CCl_4) + \tfrac{1}{2}Br_2\,(\text{in } CCl_4) && && \\
&\qquad = IBr(\text{in } CCl_4) && \Delta F^\circ_{298} = -1746\text{ cal.} && (5)
\end{aligned}$$

The final value, −1746 cal., for the free energy change accompanying reaction (5) is nearly equal to the value, −1790 cal., for the corresponding reaction where all substances are in the gaseous state. Both values are subject to an error of ±50 cal. The approximate equality of the free energies of the monobromide under these radically different conditions is of considerable interest because it indicates that the effect of the solvent on the three substances involved is much the same.

It is to be noted that the concentration units used above are mole fractions but since the equilibrium constant for reaction (5) is independent of the units used, the same constant may be employed in calculations in which the concentrations are expressed in moles per liter or moles per thousand grams of solvent. The value for the equilibrium constant for reaction (5) at 25° is 19.0 and the degree of dissociation of the iodine monobromide is 9.5%.

From the data given in Table I it is possible to determine independently, but not with great accuracy, the degree of dissociation of the iodine monobromide both in solution and in the gaseous state. The degrees of dissociation so calculated are 8 and 7% for the solution and gas, respectively, and agree satisfactorily with the corresponding more accurate] values of 9.50 and 8.9%, respectively.

In Table II are presented the thermodynamic constants of iodine monobromide. The standard reference states are indicated in each case.

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(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 516.

(6) Calculated from solubility data, Jakowkin, *Z. physik. Chem.*, 18, 588 (1895).

TABLE II

THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE AT 25°

Substance	Reference substances	Free energy, cal.
IBr (g)	I_2 (s), Br_2 (l)	903
IBr (g)	I_2 (g), Br_2 (g)	−1790
IBr (in CCl_4)	I_2 (in CCl_4), Br_2 (in CCl_4)	−1746
IBr (in CCl_4)	I_2 (s), Br_2 (l)	− 221
I_2 (in CCl_4)	I_2 (g)	−1970
IBr (in CCl_4)	IBr (g)	−1124
Br_2 (in CCl_4)	Br_2 (g)	− 366

The Stability of the Iodine Dibromide Ion, IBr_2^-

A large number of distribution experiments were made in which the solvents were carbon tetrachloride and aqueous solutions of hydrobromic and perchloric acids in order to determine the stability of the iodine dibromide ion, IBr_2^-. That there is a fairly strong tendency for the formation of this complex ion was shown by the fact that the monobromide dissolved much more freely in the hydrobromic acid than in the perchloric acid solutions. The results of experiments in which perchloric acid solutions were used showed that the reaction

$$I_2 + 5Br_2 + 6H_2O = 12H^+ + 2IO_3^- + 10Br^-$$

took place, and the bromide ion formed led to the formation of IBr_2^-. This complication rendered the values obtained for the distribution ratio of free iodine monobromide between the acid and carbon tetrachloride of doubtful significance. It is therefore impossible, at this time, to make more than a qualitative statement regarding the stability of the iodine dibromide complex. Its stability is shown roughly by the rather consistent value $300 = (IBr_2^-)/(IBr)(Br-)$, for the equilibrium constant.

Summary

The partial pressures of iodine monobromide above its carbon tetrachloride solutions have been measured at 25.0' and the constant of Henry's law, $k = p_{IBr}/N_{IBr}$, found to have the value 114 where the pressures are in millimeters.

From this result combined with known thermodynamic data it was found that the standard free energy change for the reaction $\frac{1}{2}I_2$ (in CCl_4) + $\frac{1}{2}Br_2$ (in CCl_4) = IBr (in CCl_4) is −1746 cal. at 25°. This value is nearly the same as that for the reaction $\frac{1}{2}I_2(g) + \frac{1}{2}Br_2(g) = IBr(g)$, namely, −1790 cal. The degree of dissociation of iodine monobromide in carbon tetrachloride solution is 9.5%. The standard free energy change for the reaction $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) = IBr$ (in CCl_4) at 25° is −221 cal.

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Invertase Action as a Heterogeneous Reaction

BY T. A. WHITE

Introduction

Catalysts of various sorts have been known and investigated for many years. In their efforts to determine the mechanisms by which these various agents can change the rate of a given reaction, investigators have been led to two points of view. With respect to enzymes, these points of view have resolved themselves into the question of whether the reaction is homogeneous or heterogeneous in nature. Since catalysts affect the rate of a reaction, many attempts have been made to determine the mechanism by means of reaction kinetics studies.

Most investigators in the field of enzyme action have applied the mass law to what is assumed to be a homogeneous system. This method of approach has led to an explanation of many observations that have been made by a multitude of investigators from time to time, and, consequently, has led a large group of workers to believe that enzyme reactions are homogeneous in nature. On the other hand, this method of approach has not led to a complete explanation of all the observed facts. For example, Nelson and Griffin[1] showed that not only was invertase active in solution, but it was also active while adsorbed on charcoal, demonstrating that the action may be of a heterogeneous nature. This, as well as the fact that the enzyme itself is of a colloidal nature, led Nelson and Vosburgh[2] to consider the action of invertase in hydrolyzing sucrose as a reaction of a heterogeneous rather than of a homogeneous nature. It should be mentioned, too, that Bayliss[3] also considered enzyme action as heterogeneous, and suggested that adsorption played a part in the reaction; but his views proved to be unsatisfactory. These various suggestions and methods of approach have not led to a picture which on the whole is as acceptable as that offered by Michaelis and Menten[4] from the homogeneous viewpoint.

This is due, to some extent at least, to the fact that equations which have been derived in the past from the heterogeneous viewpoint have not successfully explained the kinetics of enzyme reactions. In recent years, much progress has been made in understanding those gas reactions which take place at the surfaces of certain inorganic catalysts by recognizing that the seat of such reactions lies in the layer of adsorbed molecules on the surface of the catalyst. With invertase as an example and assuming the invertase–sucrose–water system to be heterogeneous in nature, it is the

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(1) Nelson and Griffin, THIS JOURNAL, 38, 1109 (1916).

(2) Nelson and Vosburgh, *ibid.*, 39, 790 (1917).

(3) Bayliss, *Biochem.* J., 1, 175 (1906).

(4) Michaelis and Menten, *Biochem. Z.*, 49, 333 (1913).

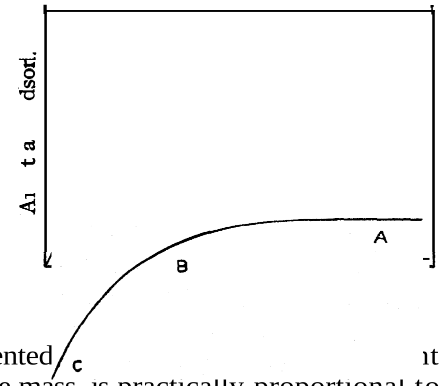
purpose of this paper to utilize these new ideas in showing that the experimental facts can be explained just as well from the heterogeneous as from the homogeneous point of view. Since the homogeneous view is so well known, and can be found discussed in full elsewhere,[5] the remainder of this paper will deal entirely with the presentation of the heterogeneous view.

Theoretical Introduction

While there is no need to give here a complete discussion of the ideas[6] that have developed around heterogeneous reactions, it may be useful to give at this time a brief survey of those principles which will later be employed in discussing the facts of invertase action. The active mass in a heterogeneous reaction is not the total amount of a given substance present, as it is in a homogeneous reaction, but is, according to the chemical adsorption theory, that part of the total mass which is actively adsorbed on the surface of the catalyst. Since only those molecules which are adsorbed by the catalyst react, the problem resolves itself into that of determining how much is adsorbed. If it be assumed that this can be more or less accurately determined by means of what is called the Langmuir[7] adsorption isotherm, which may be expressed in terms of concentration c, a constant b, and the fraction of the surface covered Θ, as

$$\Theta = \frac{bc}{1 + bc} \tag{1}$$

a number of kinetic equations may be derived. Such an adsorption isotherm may, in the general case, be represented by a curve as is shown in Fig. 1. This shows that over the section A the catalyst is completely covered, according to the theory, with a unimolecular layer of adsorbed molecules, but less and less covered at B and C. Moreover, as long as the concentration of the reactant in the solution is at a sufficiently high level to cover the surface of the catalyst with adsorbed reactant, the rate of reaction should be constant. On the other hand, over the portion represented it adsorbed, and consequently the active mass, is practically proportional to the total concentration of reactant. Under such conditions, the reaction



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[5] See Chap. V, "The Course of Enzymatic Reactions," of "Enzymes" by Haldane (1930) for a discussion of the methods employed in deriving from the homogeneous viewpoint equations which are similar to those that will be derived and used here.

[6] For a fuller discussion of these principles, see, for example: (a) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems"; (h) Taylor, "Treatise on Physical Chemistry," Chap. XV, 2d ed.

[7] Langmuir, THIS JOURNAL, 88, 2221 (1916).

should be unimolecular in nature. A reaction progressing along the section indicated by B should show an order which gradually changes from zero to unimolecular. Finally, if a reaction started in the region A, and was followed to completion, the reaction should give a constant rate, or zero order, at first, but decreasing constants thereafter, increasing unimolecular constants over the first and middle portions, and regular unimolecular constants during the last part of the reaction. In a general case, where a is the original amount of the reactant, x the amount of product at time t, k and b constants, the rate of such a reaction may be expressed as

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + b(a - x)}, \text{ or } k = 1/t \ln \frac{a}{a - x} + \frac{bx}{t} \tag{2}$$

But the above equation does not take into account the inhibiting action of the products of a reaction, and since the products do inhibit the hydrolysis of sucrose, equations should be derived to fit those conditions. The simplest case of this sort is the one that has an amount of adsorbed reactant which is proportional to the total concentration, namely, over section C of Fig. 1. Under such conditions, the amount of active mass of the reactant is equal to the product of that amount which would ordinarily be adsorbed (in this case, proportional to the total concentration of the reactant) and that fraction of the total surface which is not covered by the product. That fraction of the surface which is covered by the product is given by equation 1. The fraction of the surface which is available for the reactant is equal to

$$1 - \Theta = 1 - \frac{bx}{1 + bx} = \frac{1}{1 + bx} \tag{3}$$

Therefore, the rate under such conditions is equal to

$$\frac{dx}{dt} = \frac{k_1(a - x)}{1 + bx} \text{ or } k_2 = 1/t \ln \frac{a}{a - x} - \frac{k_3 x}{t} \tag{4}$$

Since the products inhibit the hydrolysis of sucrose with invertase, it should be expected that this equation would hold over the last part of the reaction, and it will be shown that it does.

At the beginning of the reaction, where the reactant is in sufficient concentration to cover all the surface left for it by the adsorbed product, the rate should be proportional to the product of the amount of surface available for the reactant and the amount (in this case, constant) of the reactant which would be adsorbed in the absence of any product. Thus, the rate is equal to

$$\frac{dx}{dt} = \frac{k_4}{1 + bx} \text{ or } k_4 = \frac{x}{t} + \frac{bx^2}{2t} \tag{5}$$

It will be shown that this equation holds for a considerable fraction of the invertase reaction.

The final problem, however, is to obtain a single equation that will represent the rate of hydrolysis from the beginning to the end of the reaction. In their studies of the adsorption of gas mixtures by silica, Markham and Benton[8] found that in general the fraction of the surface covered by one gas of a binary mixture followed an equation which is slightly different from equation 1. Considering the reactant and product as such a mixture, and using the same terms as before, the following equation expresses the fraction of the enzyme surface which is covered by the reactant.

$$\Theta = \frac{b(a - x)}{1 + b(a - x) + cx} \tag{6}$$

Under such conditions, therefore, the rate is equal to

$$\frac{dx}{dt} = \frac{k_5(a - x)}{1 + b(a - x) + cx} \text{ or } k_5 = \frac{1 + ac}{t} \ln \frac{a}{a - x} + \frac{(b - c)x}{t} \tag{7}$$

It will be noticed that equation 7 may be reduced to the same form as equation 2. Perhaps it is for this reason that various workers have found that the course of the reaction agreed well with equation 2, which was obtained by others from the homogeneous viewpoint as well as here without considering the products. Further, it should be pointed out that equation 7 reduces to equation 4 toward the end of the reaction, where the value of $b(n - x)$ becomes small in comparison with the other terms.

Experimental Methods

Before the actual results are presented, the methods and types of apparatus employed will be recorded. While no new or unusual methods were used, all recognized methods for obtaining accurate results were carefully observed as far as was possible. The details of such methods are as follows.

The sucrose used in these experiments was prepared by recrystallizing ordinary cane sugar at room temperature by adding enough absolute ethyl alcohol to a saturated water solution of cane sugar to make the concentration of alcohol about 75% by volume. The precipitated sucrose was filtered off, washed several times with absolute alcohol, and dried at room temperature. Fresh solutions were prepared from this preparation just before a hydrolysis was begun by adding to the necessary amount of sugar 25 cc. of buffer and enough distilled water to make the volume 500 cc.; 400 cc. (half quantities were sometimes used) of this solution was placed in a glass-stoppered bottle and allowed a half hour to come to temperature equilibrium in a water thermostat. accurate to ±0.02°, before the reaction was started by pipetting a given quantity of enzyme into the reaction solution. Twenty cc. samples were pipetted from the reaction mixture and run into 5 cc. of 0.2 *M* sodium carbonate at room temperature in order to stop the reaction and to hasten mutarotation. Two drops of 40% sodium hydroxide were used instead of the sodium carbonate in the case of 3% sugar solutions. The delivery time of the pipet was ten seconds, and the mean of this value was taken as the time of taking the sample.

Two buffer solutions were used: P_H 4.7 was obtained with a 0.1 N sodium acetate–acetic acid solution, and P_H 6.4 and 7.4 were obtained with Clark and Lubs'[9] acid potassium phosphate–sodium hydroxide buffer solutions. The invertase was prepared from yeast according to the method suggested by Morrow,[10] and a 2.6% solution was used.

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(8) Markham and Benton, THIS JOURNAL, 53, 497 (1931).

(9) See Clark, "The Determination of Hydrogen Ions," 1928, 3d ed., p. 192.

10) Morrow, "Biochemical Laboratory Methods," 1927, p. 281.

All readings were taken at room temperature in a 2-dm. tube. **A** high grade, triple-field Schmidt and Haensch polarimeter, calibrated to **0.01°**, was employed. While the room temperature varied from day to day by as much as four degrees, such changes were followed, and it is believed that they did not produce trends in the readings, for all readings were generally made within a narrow temperature range. A *Lab Arc*, with a Corning Glass filter to give the **5461 Å.** line, was used as a light source. Rotations due to strains in the cover glasses were avoided by rotating the tube between readings. Readings were always taken until mutarotation was complete, as indicated by the constancy, within **0.01'**, of polarimetric readings over a period of ten minutes. The initial rotation was synthetically determined by taking **20** cc. of a mixture of the original sugar solution with a proportionate amount of water to correspond to the amount of invertase which was added to the reaction solution. The invertase had no measurable optical activity. After allowing the reaction to run for one or two days, the rotation at the end of that time was considered as the final value. These values agreed within the experimental error with the theoretical amounts. The initial concentration of the sucrose, in terms of degrees of rotation, was taken as the initial rotation minus the final rotation; and the concentration of the sucrose at any time t was taken as the rotation at that time minus the final rotation.

Experimental Results

The Beginning of the Reaction.—It was found, as so many investigators have found, that the initial part of the hydrolysis proceeded with a constant rate, and continued to do so up to about ten per cent. hydrolysis. If the products did not inhibit the reaction, one would expect the rate to remain constant so long as the amount of sucrose adsorbed by the invertase is constant; but with the products inhibiting the reaction, the rate, under normal conditions, should gradually fall off. Equation 5 was derived to fit these conditions, and the following values in Table I show that the equation holds over a considerable portion of the reaction. Other values will be found in column 6 of Table IV.

TABLE I

RESULTS FOR 25° AND P_H 4.7

Run 9: 1.0 cc. enzyme per 400 cc. of 6% sucrose				Run 11: 1.0 cc. enzyme per 400 cc. of 10% sucrose			
Time. min.	x °Rot.	% Hydro.	$k = \frac{x}{t} + \frac{0.045x^2}{t}$	Time, min.	x °Rot.	% Hydro.	$k = \frac{x}{t} + \frac{0.013x^2}{t}$
0	0.00	0.0	...	0	0.00	0.0	...
10	1.26	12.9	0.133	15	1.70	10.5	0.116
20	2.42	24.8	.134	30	3.37	20.8	.117
40	4.44	45.4	.133	60	6.50	40.2	.117
60	6.10	62.3	.130	90	9.06	56.0	.113
90	7.82	79.9	.128	120	11.14	68.9	.106
∞	9.79	..	...	m	16.19	..	...

Different Amounts of Enzyme.—Figure **2** gives a series of curves which shows how the unimolecular constant, as calculated from $k_m = l/t \log a/(a - x)$, varies as the reaction progresses. It will be noticed that the constants increase until about 93.5% of the sucrose has been hydrolyzed, and then decrease over the remainder of the reaction. Since the temperature, PH, sucrose concentration, and water concentration were the same, and only the amount of enzyme was varied in these experiments, it must be concluded that the maxima, which come at approximately 93.5% hydrolysis in all the cases, are independent of the amount of enzyme present.

The well-recognized fact that the rate of hydrolysis for a given concentration of sucrose is proportional to the concentration of enzyme present is also illustrated in the curves. This would be expected, for the enzyme will adsorb twice as much of the reactant as half that amount of enzyme will adsorb under the same conditions, and, since the rate is proportional to the amount of reactant adsorbed by the catalyst, the rate of hydrolysis should be twice as great in the former as in the latter case.

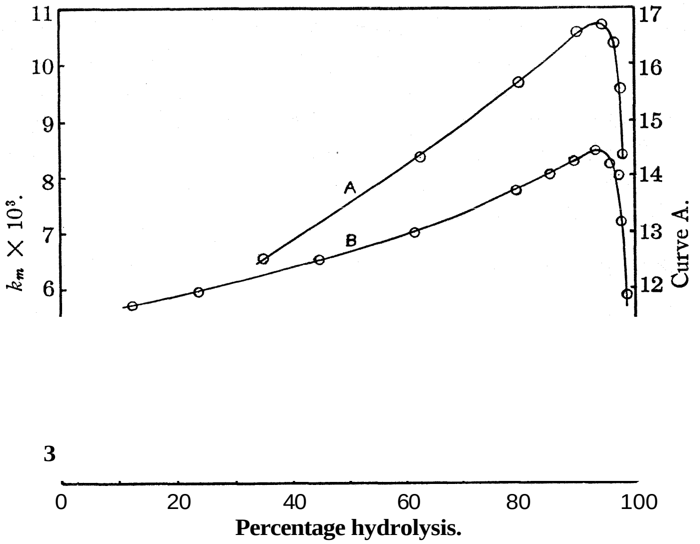

Fig. 2.—400 cc. of 6% sucrose, PH 4.7, 25°, with varying amounts of enzyme: Curve A, run 10, 2.0 cc. of invertase; Curve B, run 13, 1.0 cc. of invertase; Curve C, run 12, 0.5 cc. of invertase.

Different Amounts of Sucrose.—It will be noticed that the curves of Fig. 3 show the same general properties as those of Fig. 2. On the other hand, the additional fact is brought out that while the unimolecular constant goes through a maximum at a definite per cent. hydrolysis for a given initial sucrose concentration, irrespective of the amount of enzyme present, each sugar solution gives a maximum which depends on the initial concentration of the sugar. The maximum comes at 96% hydrolysis for 10% sucrose, at 93.5% hydrolysis for 6% sucrose, and at about 90% hydrolysis for 3% sucrose. These values indicate that the unimolecular constant goes through the transition period when the amounts of sucrose present in the solution are 0.40, 0.39, and 0.30%, respectively.

Different *Ph* Values.—Besides the very interesting fact that the rate of hydrolysis markedly decreases with an increase in the Ph of the solution from 4.7 to 7.4, the curves of Fig. 4 also show that the unimolecular constant goes through a maximum at different percentages of hydrolysis for different values of Ph. For 6% sucrose solutions, the maximum occurs at 93.5% hydrolysis for Ph 4.7, at **91.5%** hydrolysis for *Ph* **6.5,** and at **86.5%** hydrolysis for Ph 7.4. From these values, therefore, it must be concluded that besides decreasing the amount of sucrose adsorbed by the invertase, as indicated by a decrease in rate, an increase in Ph from 4.7 to 7.4 also modifies the general shape of the adsorption isotherm so that the isotherm reaches its saturation value at higher sucrose concentrations with higher values of Ph. It is not known how the surface of the enzyme particles varies with Ph, but it seems reasonable to suppose that the active surface varies considerably with *Ph*; and hence contributes to the above mentioned variations.

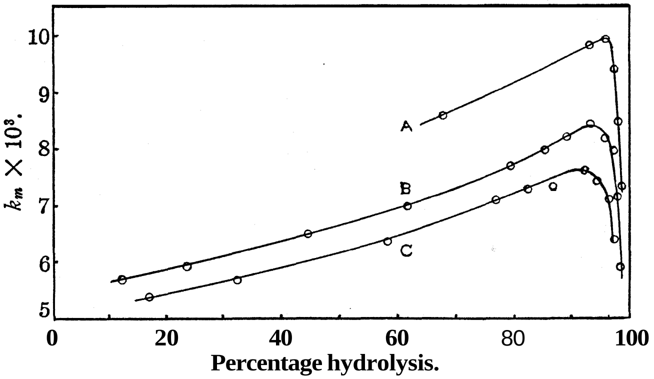

Fig. 3.--400 cc. of sucrose, Ph 4.7. 25°, with varying sucrose concentrations: Curve A, run 17, 10% sucrose, 2.0 cc. of invertase; Curve B, run 13, 6% sucrose, 1.0 cc. of invertase; Curve C, run 15, 3% sucrose. 0.5 cc. of invertase.

Effect of Temperature.—It is a well-recognized fact that the higher the temperature the higher the concentration at which an adsorption isotherm reaches its saturation value. In view of this fact one would expect that. for a given initial sucrose concentration and at the same Ph, the maximum of the unimolecular versus percentage hydrolysis curve would come at a lower percentage of hydrolysis the higher the temperature. The curves of Fig. 5 show that this is actually the case; for, if the curves of Fig. 5 are compared with those of Fig. 4, it will be noticed that with an initial sucrose concentration of 6% the maximum is shifted from 93.5% hydrolysis to 89.0% hydrolysis at Ph 4.7, and from 86.5% hydrolysis to 75.0% hydrolysis at Ph 7.4, for a ten degree rise in temperature. It should be pointed out that, since the dispersion of colloids is affected by temperature, some of this change is probably due to a change in the enzyme surface.

The End of the Reaction.—Throughout the results that have been given, it has been assumed that the variations of the unimolecular constant with percentage hydrolysis are real and that they are the result of the reaction itself. Previous investigators[11] have obtained one or a few unimolecular constants which showed a decreasing tendency toward the end of the reaction, but they have neglected them as due to a destruction of the enzyme by means of heat or as due to experimental error. The fact that

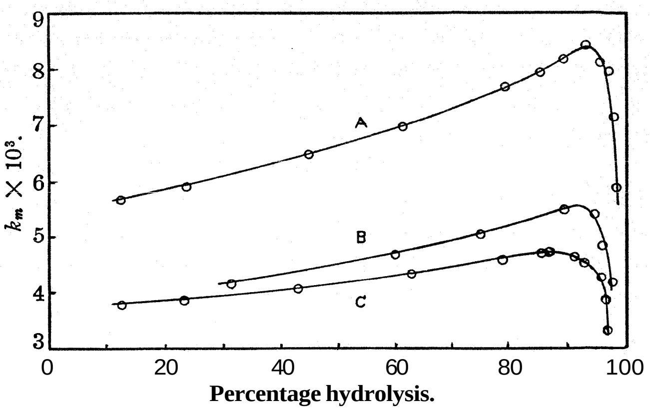

Fig. 4.—400 cc. 6% sucrose, 25°, at various P_H values: Curve A, run 13. P_H 4.7, 1.0 cc. of invertase; Curve B, run 19, P_H 6.5 1.0 cc. of invertase; Curve C, run 21, P_H 7.4, 4.0 cc. of invertase.

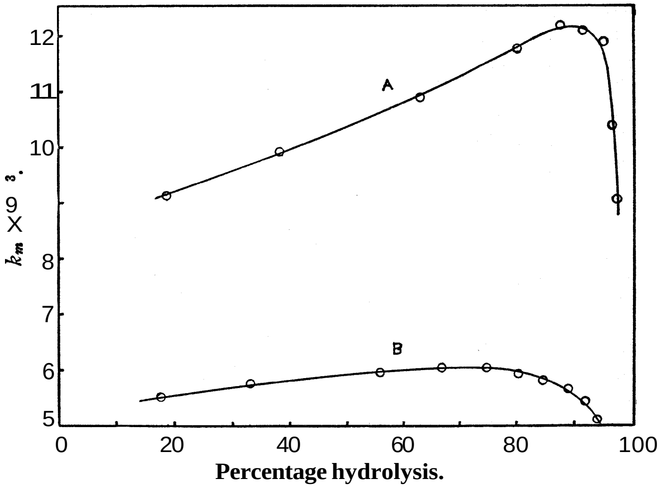

Fig. 5.—400 cc. 6% sucrose, 35°: Curve A, run 25. P_H 4.7, 1.0 cc. of invertase; Curve B, run 24, P_H 7.4, 4.0 cc. of invertase.

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(11) Auden and Dawson, *Biochem. J.*, 25, 1909 (1931).

the maximum in the unimolecular constants for a given initial sucrose concentration comes at the same percentage hydrolysis, irrespective of the velocity of conversion, indicates that the enzyme is not destroyed at the temperatures used in this investigation. On the other hand, while it must be said that the experimental error toward the end of the reaction is larger than at the beginning, it is felt that a much larger error than was actually present would have to be assumed in order to change the general trend of the curves. The most striking part of the curves, however, is the definiteness with which the unimolecular constant decreases toward the end of the reaction. It is for this last part of the reaction that equation 4 was derived to fit Due to the fact that only a few points could ordinarily be obtained within this range of hydrolysis, only a few constants could be calculated.

TABLE II

RESULTS FOR 25" AND PH 4.7

	Run 12: 0.5 cc. enzyme per 400 cc. 6% sucrose				Run 17: 2.0 cc. enzyme per 400 cc. 10% sucrose		
Time, min.	$a - x$ °Rot.	$k_m = 1/t \log \frac{a}{a-x}$	$k = k_m - \frac{0.05x}{t}$	Time, min.	$a - x$ °Rot.	$k_m = 1/t \log \frac{a}{a-x}$	$k = k_m - \frac{0.069x}{t}$
0	9.79	.....	.....	0	16.21	.....	.....
15	8.95	0.00260	.....	60	5.19	0.00859	.....
30	8.04	.00285	.....	120	1.08	.00980	.....
60	6.41	.00307	.....	140	0.66	.00993	0.00234
90	4.96	.00328	.....	170	.41	.00939	.00299
135	3.21	.00356	.....	210	.27	.00847	.00324
180	2.00	.00383	.....	270	.17	.00733	.00323
220	1.30	.00399					
250	0.95	.00405	.....				
280	.70	.00409	0.00247				
310	.54	.00406	.00257				
350	.42	.00391	.00257				
410	.29	.00373	.00257				

TABLE III

RESULTS FOR 35°

	Run 24: PH 7.4; 4.0 cc enzyme per 400 cc. 6% sucrose				Run 25: PH 4.7; 1.0 cc. enzyme per 400 cc. 6% sucrose		
Time, min.	$a - x$ °Rot.	$k_m = 1/t \log \frac{a}{a-x}$	$k = k_m - \frac{0.033x}{t}$	Time, min.	$a - x$ °Rot.	$k_m = 1/t \log \frac{a}{a-x}$	$k = k_m - \frac{0.089x}{t}$
0	9.73	.....	.....	0	9.85	.....	.....
15	8.05	0.00549	.....	10	7.99	0.00909	.....
30	6.54	.00575	.....	21	6.10	.00991	.....
60	4.28	.00594	.....	40	3.63	.01084	.....
80	3.22	.00600	.....	60	1.95	.01172	.....
100	2.43	.00603	.....	75	1.21	.01214	.....
120	1.90	.00591	0.00376	90	0.81	.01205	0.00310
140	1.50	.00578	.00384	110	.49	.01185	.00428
170	1.07	.00564	.00396	140	.35	.01035	.00431
200	0.80	.00543	.00396	180	.23	.00906	.00431
240	.60	.00504	.00378				

However, the values in Tables II, III and IV show that equation 4 holds remarkably well.

Summary of Results.—In the preceding sections, it has been pointed out that the velocity of hydrolysis is constant for about the first 10% hydrolysis, but later decreases; that the unimolecular constant increases to a maximum and then decreases as the reaction progresses; that this maximum value changes in a regular manner with P_H, temperature, and initial concentration of sucrose, but not with the amount of enzyme present; and, finally, the various equations which were derived in the theoretical introduction have been applied to the data. As a final summary of the results, however, Table IV shows how those equations hold for a single hydrolysis. It will be noticed that equation 7 holds fairly well over most of the reaction, that equation 4 holds over the last part of the reaction, and that equation 5 holds well over the first half of the reaction. In other words, each equation holds over that part of the reaction which it is theoretically supposed to fit.

TABLE IV

RUN 2 AT 25° AND P_H 4.7: 0.5 CC. OF ENZYME PER 400 CC. OF 6% SUCROSE

Time, min.	$a - x$ °Rot.	% Hydro	$k_m = 1/t \log \frac{a}{a - x}$	$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$	$k = \frac{x}{t} + \frac{0.0048x^2}{t}$	$k = k_m + \frac{0.035x}{t}$	$k = k_m - \frac{0.0095x}{t}$
0	9.82	0.0	.....	.....	....	.....	.....
5	9.46	3.7	0.00324	0.00324	0.0732	0.00576	.....
15	8.76	11.8	.00331	.00337	.0743	.00579	.....
30	7.78	20.8	.00337	.00333	.0747	.00575	.....
40	7.23	26.4	.00343	.00318	.0729	.00570	.....
60	6.08	38.1	.00347	.00376	.0735	.00565	.....
90	4.55	53.4	.00371	.00419	.0734	.00576	.....
120	3.33	66.1	.00391	.00452	.0710	.00580	.....
180	1.67	83.0	.00427	.00483	.0656	.00586	.....
240	0.86	91.4	.00441	.00464	....	.00572	0.00406
270	.63	93.5	.00438	.00451	....	.00561	.00405
300	.48	95.2	.00437	.00393	....	.00546	.00407
330	.38	96.2	.00428	.00338	....	.00528	.00401

General Discussion

The Role of Water.—The foregoing results are in agreement with the recognized fact that the initial velocity of hydrolysis increases to a maximum as the initial sucrose concentration is increased to about 6%, and declines as the sucrose concentration is increased above that amount. Nelson and Schubert[12] showed that the velocity of hydrolysis for strong sucrose solutions decreased as the water concentration decreased, and stated "that the concentration of water is a factor in determining the magnitude of hydrolysis of sucrose by invertase," but they did not show how the water is a determining factor. While Henri[13] regarded the enzyme as containing

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(12) Nelson and Schubert, THIS JOURNAL, **50**, 2188 (1928).

(13) Henri, *Z. physik. Chem.*, **51**, 27 (1905).

some of the water, it seems that water, as a controlling factor in determining the velocity of hydrolysis, has been rather generally neglected. Moreover, following the views of Michaelis and Menten,[4] it has become customary to explain the increase in initial velocity up to about 6% sucrose concentration as due to increasing amounts of sucrose combined with the enzyme. On the other hand, investigators seem to have forgotten the fact that the initial velocity during this range of sucrose concentration is zero order, and that the velocities can only be of that order when the enzyme is saturated with respect to sucrose, which, according to the views of Michaelis and Menten, is the case only at considerably higher sucrose concentrations.

From the chemical adsorption view, which requires that both the water and the sucrose must be adsorbed before the enzyme can influence the velocity of the combination, water occupies a special position. Except in solutions with high sucrose concentrations, water is always present in large excess. Consequently, the amount of water used up in a given reaction is negligible, and, hence, the amount of water adsorbed by the enzyme remains essentially constant. Therefore, for a given hydrolysis, water plays no important part in the manner in which the velocity changes as the hydrolysis proceeds. On the other hand, since the amount of water present does vary from one initial sucrose concentration to another, water does play an important part in determining the velocity with which the hydrolysis will go at different initial sucrose concentrations.

If it be assumed that water is adsorbed in preference to sucrose, the facts can be explained in this manner. Water molecules will then be adsorbed and will cover the surface of the invertase according to their concentration; and sucrose molecules will saturate, even at quite low sucrose concentrations, that part of the surface which is not covered by water. At low (less than 6%) initial sucrose concentrations, where the water concentration is high, more water is adsorbed than sucrose; but at high (greater than 6%) initial sucrose concentrations, where the water concentration is lower, more sucrose and less water are adsorbed. The maximum velocity would occur at an optimum ratio of adsorbed sucrose to adsorbed water, and the velocity should fall off from this value for both higher and lower initial sucrose concentrations. Furthermore, on the basis of such a mechanism, it is possible for the amount of adsorbed sucrose to reach a saturation value for practically any initial sucrose concentration, and, hence, give a constant rate at the beginning of each hydrolysis.

Inhibition.—The manner in which invert sugar inhibits the hydrolysis deserves special mention. It has been pointed out that the reaction proceeds as a zero order reaction for about the first 10% of hydrolysis. This indicates that the products of the reaction are not adsorbed by the invertase and do not inhibit during that time, for they could only inhibit the reaction by occupying some of the enzyme surface which would ordinarily be active. At least three factors contribute to this delay in the inhibition of the reaction: first, the mutarotated or β-forms of the invert sugar inhibit to a greater degree than the α-forms;[14] second, the slow rate of transformation of the a-form to the β-form produces at a given time a smaller quantity of the inhibiting substances than the equilibrium amount;[15] third, the inhibiting substances may not only be slowly adsorbed, but there may be an induction period before adsorption occurs.[16] All of these factors would be more noticeable at the beginning of the reaction, because there the velocity of the hydrolysis reaction is at its maximum, mutarotational velocities are slowest, and the products (in the presence of large quantities of sucrose) would have more difficulty in being adsorbed by the invertase.

On the other hand, it must not be forgotten that these factors should also be considered during the entire reaction in determining the correct concentration of products which are responsible for the inhibiting action at a given time. In view of the many factors controlling the amounts of products which are adsorbed by the enzyme, it is somewhat surprising that equations 4 and 5 hold as well as they do. However, over a short portion of the hydrolysis, and especially toward the end of the reaction where the rate factors are favorable, the amounts of inhibiting substances which are active are probably more or less proportional to the total quantity of products present. While equation 7 does not fit over the entire reaction, it does express the course of the reaction remarkably well. It is quite possible that the Langmuir isotherm does not fit over the entire range, and, hence, is the root of the difficulty; but it is more probable that most of the trouble is due to an unaccountable variation in the inhibiting action of the various products. Moreover, it is absolutely necessary to know what the concentrations are of those products which inhibit at any given time during the hydrolysis in order to develop for the reaction a theoretical equation that will fit from the beginning to the end of the reaction.

Summary

1. Assuming that sucrose and water are adsorbed by invertase and that the seat of the reaction is in this adsorbed phase, a theoretical treatment of the kinetics of the reaction has been given from that point of view.

2. It has been shown that the unimolecular constants increase at first as the reaction progresses, and then decrease toward the end of the reaction. The influence of the amount of enzyme, PH, initial sucrose concentration, and temperature on this maximum is shown.

3. An explanation of the role water plays in influencing the initial velocity of hydrolysis has been advanced.

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(14) For example, see Nelson and Bodansky, THIS JOURNAL, 47, 1624 (1925).

(15) Compare with Pennycuick, *J. Chem. Soc.*, 125, 2049 (1924).

(16) The recent results of Benton and White [THIS JOURNAL, 54, 1820 (1932)] with hydrogen and iron indicate that an induction period is possible in the adsorption process.

4. The inhibiting action of the products and its importance in obtaining a general kinetic equation for the reaction has been discussed.

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The Debye-Hückel Ion Size Parameter in Terms of Individual Ionic Radii. The Activity Coefficient of Lead Chloride in Solutions of Cadmium Nitrate[1]

BY H. D. CROCKFORD AND HENRY C. THOMAS

In the past the ion size parameter of the Debye-Hiickel theory of solutions of strong electrolytes has been determined as a mean value for the ions of a given solution. If the parameter "*a*" could be calculated from the individual ionic radii and the result of this calculation verified experimentally, the physical meaning of the quantity "*a*" would take on added significance. It is the purpose of this paper to present this calculation and to give a preliminary test of its result.

Theoretical Calculation.—Consider a solution containing ions of kinds

$$1 \ldots i \ldots s$$

Let a_{ij} be the mean distance of closest approach for the ions of the i^{th} and j^{th} kinds, *i*. e., the mean collision distance between the centers of the ions considered as spheres. Now if f_{ij} is the time average, or frequency, of collisions between the ions of the i^{th} and j^{th} kinds, then

$$\text{"}a\text{"} = \Sigma f_{ij}a_{ij}/\Sigma f_{ij} \qquad (1)$$

is the mean distance of closest approach for all ions in the solution, the summations being taken over all combinations of values of i and j. On the average for a large number of random collisions between any two ions the distances from the points of contact to their centers may be considered as the radii of spheres surrounding the ions; so that

$$a_{ij} = a_i + a_j$$

The quantities a_i and a_j depend presumably only upon the nature of the individual ions.

The following calculation of the frequency of collisions between the ions is based on the fundamental assumption of the Debye-Hückel theory: the effects between the ions may be attributed wholly to the electrical charges on them. Consider an ion of the i^{th} kind in a solution of

$$n_1 \ldots n_i \ldots n_s$$

moles of ions with valences

$$z_1 \ldots z_i \ldots z_s$$

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[1] The material for this paper was taken from a thesis submitted by Henry C. Thomas to the Faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Master of Science.

dissolved in a volume V of solution. The charge on an ion of the i^{th} kind is then $z_i\epsilon$, where ϵ is the charge on the electron. If dV is an elementary volume of solution at a distance r from an ion of the i^{th} kind, the time average of the number of ions of the j^{th} kind in dV is given by the Boltzmann relation

$$\frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, dV$$

N is Avogadro's number per mole, Nn_j/V being the number of ions of the j^{th} kind per cubic centimeter of solution; ψ, the electrical potential in dV; k, Boltzmann's constant; T, the absolute temperature; and e, the base of the natural logarithms. On changing to space polar coordinates and performing the indicated integration, there is obtained the number of ions of the j^{th} kind in a spherical shell of thickness dr surrounding and at a distance r from the i^{th} ion in question

$$\frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, r^2 dr \int_0^{\pi}\int_0^{2\pi} \sin\theta\, d\theta\, d\phi = 4\pi \frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, r^2 dr$$

In order to calculate the time average of collisions between the ion of the i^{th} kind and all the ions of the j^{th} kind, the above expression is integrated through a shell in contact with the i^{th} ion and of such thickness, $2a_j$, that all the ions of the j^{th} kind within the shell must be in contact with the i^{th} ion. Multiplying the resulting expression by the number of ions of the i^{th} kind per cubic centimeter, there is obtained the time average of all collisions per cubic centimeter between ions of the i^{th} and j^{th} kinds

$$f_{ij} = \frac{4\pi N^2}{V^2}\, n_i n_j \int_{a_i}^{a_i+2a_j} e^{-z_j\epsilon\psi/kT}\, r^2\, dr$$

When this expression is summed over all pairs of kinds of ions in solution, the result is the time average, or frequency, of all collisions per cubic centimeter

$$\sum f_{ij} = \frac{4\pi N^2}{V^2} \sum_{i=1}^{s} \sum_{j=1}^{s} n_i n_j \int_{a_i}^{a_i+2a_j} e^{-z_j\epsilon\psi/kT}\, r^2\, dr \qquad (2)$$

In order to obtain this expression in terms of the concentration of the dissolved compound we note that $n_i = \nu_i n$, where n is the number of moles of the compound in volume V of solution and ν_i the number of ions of the i^{th} kind to which one molecule of salt gives rise on ionization. The potential ψ at large distances from an ion is to be determined from the general solution of the Poisson–Boltzmann equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi_i}{dr}\right) = -\frac{4\pi\epsilon}{D} \sum_{j=1}^{s} \frac{Nn_j z_j}{V}\, e^{-z_j\epsilon\psi_i/kT}$$

However, in calculating the frequency of collisions only the potential near the surface of the ion is considered. The potential in this neighborhood will be largely due to the charge on the ion itself. Therefore no large error will be introduced if the potential is considered as arising wholly from the charge on the ion

$$\psi = \frac{z_i\epsilon}{D}\frac{1}{r} \tag{3}$$

where D is here the dielectric constant of the solvent. On making these substitutions the expression for the frequency becomes

$$\sum f_{ij} = 4\pi N^2 \left(\frac{n}{V}\right)^2 \sum_{i=1}^{s} \sum_{j=1}^{s} \nu_i\nu_j \int_{a_i}^{a_i+2a_j} e^{-z_iz_j\epsilon^2/DkTr}\, r^2\mathrm{d}r \tag{4}$$

Substituting (3) for the potential receives justification when it is observed that if the integral in (2) should contain concentration terms other than as a factor, the "*a*" value, see (1), would depend on the concentration of the solution. This is contrary to experimental knowledge. Were the potential determined by a solution of the Poisson–Boltzmann equation, concentration terms would enter otherwise than as a factor.

The frequency of collisions between the ions of a single salt in solution is then, in the region of dilute solutions, directly proportional to the square of the concentration.

For a solution of two salts the mean distance of closest approach will be given by an expression of the form

$$\text{“}\bar{a}\text{”} = \frac{A_1 + A_2}{f_1 + f_2} \tag{5}$$

Here A_1/f_1 = "a_1" and A_2/f_2 = "a_2"; the subscripts refer to the values for the individual salts. Expression (5) is the mean of "a_1" and "a_2" in which the separate values are weighted according to the corresponding collision frequencies. This expression may be considered as a close approximation to the value of "$\bar{a}$" given by (1), where the summations are carried over all combinations of *i* and *j*. We have now

$$f_1 = k_1\left(\frac{n_1}{V}\right)^2 = k_1c_1^2 \text{ and } f_2 = k_2\left(\frac{n_2}{V}\right)^2 = k_2c_2^2$$

where k is the coefficient of the concentration term in (4) and c is the molarity of the dissolved salt. Expression (5) shows that the "$\bar{a}$" value of a solution of two salts should remain constant if the ratio of the concentrations of the salts is held constant no matter what the total concentration may be. This fact is at once apparent when (5) is written in the form

$$\text{“}\bar{a}\text{”} = \frac{K_1c_1^2 + K_2c_2^2}{k_1c_1^2 + k_2c_2^2} = \frac{K_1b + K_2}{k_1b + k_2}$$

where b = $(c_1/c_2)^2$ = const. These considerations hold true, of course, only for dilute solutions of completely dissociated electrolytes.

Now the proportionality constants k_1 and k_2 will not in general be the same for different salts. If, however, the salts are of the same valence type, the difference between these constants will be determined solely by the integral in (4). In the following discussion, due to lack of any definite knowledge of the ionic radii, we will assume $k_1 = k_2$; so that

$$f_1/f_2 = (c_1/c_2)^2 \tag{6}$$

A rough graphical integration of the function

$$r^2e^{-z_1z_2\epsilon^2/DkTr}$$

for a **1–2** salt in water at 25° shows that for values of r between 4 **Å.** and 10 **Å.** the difference between the integrals for similar types of salts should not be large. With expressions **(5)** and **(6)** it is a simple matter to calculate any one of "a_1," "a_2" or "a," given two of them.

As an experimental test of the above ideas the results of measurements on the cell

$$\text{Pb–Hg (2 phase)} \mid PbCl_2(m_1),\ Cd(NO_3)_2(m_2) \mid AgCl\text{–}Ag;\ m_1/m_2 = \text{const.}$$

have been applied. The "a" value of lead chloride has been calculated by La Mer, Gronwall and Greiff[2] from measurements by Carmody[3] on a similar cell containing only lead chloride. They find "a_1" = **1.75 Å.** The "a" value for cadmium nitrate has been calculated by the present authors from freezing point measurements of Jones,[4] these being apparently the only available measurements on cadmium nitrate in sufficiently dilute solution. Too much reliance cannot be placed on the results of these calculations, based as they are on data of doubtful precision. Table I gives the results of these calculations.

TABLE I

Molarity	Δt_f obs.	Δt_f "a" = 8.0 Å.	Δt_f "a" = 11.5 Å.	Δt_f "a" = 14.0 Å.
0.001000	0.0054	0.0054	0.0054	0.0054
.002980	.0159	.0157	.0158	.0159
.004920	.0261	.0257	.0260	.0261
.006900	.0362	.0358	.0362	.0364
.00876	.0457	.0453	.0458	.0461
.02000	.1035	(.1000)	(.1038)	(.1046)

As may be seen the value "a_2" = **11.5 Å.** gives the best agreement with the experimental data. The Debye first approximation for the osmotic deviation

$$\Theta = 0.764\sqrt{3c}\ \sigma(K\text{“}a\text{”})$$

was used in the calculation, the "a" value being sufficiently high to warrant the use of the simple equation.

Experimental Part

Purification of Materials.—Kahlbaum lead chloride was recrystallized three times from 0.006 N hydrochloric acid as recommended by Baxter and Grover.[5] **The product**

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(2) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

(3) Carmody, THIS JOURNAL, 61, 2905 (1929).

(4) Jones, *Z. physik. Chem.*, **11**, 545 (1893).

(5) Baxter and Grover, THIS JOURNAL, **37**, 1061 (1915).

was carefully dried and ground. Kahlbaum cadmium nitrate was recrystallized three times from water. Carefully purified mercury was twice distilled as recommended by Hulett.[6] Commercial tank nitrogen was purified by passing it through a solution of acidified potassium permanganate and further treated according to Cowperthwaite and La Mer.[7]

Analytical.—The stock solution of lead chloride was analyzed by the potentiometric titration of the chloride using a silver-silver chloride indicator electrode and a 0.1 *N* calomel half cell with an ammonium nitrate–agar gel bridge. The cadmium nitrate solution was analyzed by electrolytic precipitation from an alkaline cyanide bath.

Preparation of Electrodes.—The silver–silver chloride electrodes were prepared according to the method described by Carmody.[8] The lead amalgam was prepared by dissolving Kahlbaum stick lead, "for analysis" grade, sufficient to make a 6% amalgam, in the purified mercury. After solution had been effected in an atmosphere of nitrogen, the amalgam was drawn into a Pyrex storage bulb similar to that described by La Mer and Parks.[9]

Preparation of Solutions.—The solutions for measurement were made up by diluting the analyzed stock solutions of lead chloride and cadmium nitrate using flasks calibrated to deliver by the Bureau of Standards.

Electrical Apparatus and Cell Vessel.—The potentiometer, which had been calibrated by the Bureau of Standards, was the Type K instrument of Leeds and Northrup. A Leeds and Northrup No. 2500, Type R, galvanometer was used. The standard cell. also calibrated by the Bureau of Standards, was of the Weston unsaturated type. The electrical measuring apparatus was protected against electrical leakage by equipotential shielding. The cell vessel, constructed of Pyrex glass, contained two sets of electrodes. The e. m. f. of each of the four combinations was measured. A reservoir for the solution was attached so that check measurements could be obtained without disturbing the electrodes or opening the cell to the air. The nitrogen served to stir the solution and preserve an inert atmosphere within the cell. No trouble was experienced in obtaining e. m. f. readings constant to 0.02 mv. The cell was placed in a water thermostat at 25 ± 0.02°. The Beckmann thermometer was compared with a thermometer calibrated by the Bureau of Standards.

Results and Calculations

Table II gives a summary of the experimental data together with the activity coefficient of the lead chloride, γ_s, calculated from the equation

$$E_{(\text{mv.})} + 88.725\,(0.2007 + \log m) = E_{0(\text{mv.})} - 88.725 \log \gamma_s$$

this being the equation for a chemical cell without transference after the constants for a 1–2 salt at 25° have been introduced. The value E_0 =

TABLE II

	m $PbCl_2$	m $Cd(NO_3)_2$	E. m. f., volts	γ_s
1	0.01633	0.01738	0.5174	0.420
2	.01020	.01086	.5295	.491
3	.006527	.006946	.5420	.555
4	.004665	.004965	.5516	.605
5	.003263	.003471	.5623	.655
6	.002040	.002170	.5767	.721

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(6) Hulett. *Phys. Rev.*, **23**, 314 (1911).

(7) Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931)

(8) Carmody, *ibid.*, **51**, 2901 (1929).

(9) La Mer and Parks. *ibid.*, 53, 2040 (1931).

0.3432 volt calculated by La Mer, Gronwall and Greiff[2] from Carmody's[3] results was used in the calculations, The values given for the e. m. f. cannot be considered reliable to much better than 0.3 mv.

The values of γ_s here given are uniformly lower than those given by Carmody for lead chloride in solution alone.

The "$\bar{a}$" values for the four most dilute solutions have been calculated from the Debye first approximation for the activity coefficient

$$-\log \gamma_s = \frac{1.53636\,(-z_1z_2)K}{1 + \text{“}\bar{a}\text{”}K}$$

For solutions of a 1–2 salt in water at 25° $K = 0.5686\sqrt{m}$; m is here the total molality. For solutions of this dilution it is unnecessary to distinguish between molality and molarity. Since cadmium nitrate and lead chloride are of the same valence type, the only effect which the presence of cadmium nitrate has on the calculations is to increase the value of K. In this connection see La Mer, Gronwall and Greiff,[2] p. 2282

The results of these calculations are given in Table III.

TABLE III

No.	3	4	5	6
10^{-8} K	0.06599	0.05580	0.04666	0.03689
"$\bar{a}$," Å.	3.16	3.76	4.70	6.44

Discussion of Results

As is shown in Table III the "$\bar{a}$" values for mixed solutions of lead chloride and cadmium nitrate at constant ratio of concentration are not constant but increase with decreasing concentration. On the basis of our theoretical discussion this phenomenon would not be expected in such solutions of two strong electrolytes. In the case, however, of solutions containing cadmium and chloride ions this drift in the "$\bar{a}$" values may be accounted for very simply. It has long been recognized that cadmium chloride possesses many of the properties of a weak electrolyte. This salt may not be regarded as completely dissociated even at concentrations as low as 0.0005 m. The cadmium ion is presumably the component of cadmium nitrate which gives rise to its large, 11.5 Å., "a" value. If the cadmium ion is removed from the solution as undissociated cadmium chloride, it becomes in effect a part of the solvent and no longer exerts any influence on the mean distance of closest approach of the ions in the solution. As the dilution increases the cadmium chloride becomes more and more dissociated, and, due to the presence of more cadmium ion in solution, the "a" value increases. A consequence of this idea is that the solution should have a "normal" "$\bar{a}$" value at infinite dilution. When the "a" values given in Table III are plotted against the concentration, the values for the three most dilute solutions fall on a straight line. On extrapolating this line to zero concentration the limiting "$\bar{a}$" value is found to be 6.8 Å. Assuming the value of 6.8 Å. for the mean distance of closest approach of the mixed solutions, the value of 1.75 Å. for lead chloride and using expressions (5) and (6) the "a_2" for cadmium nitrate is calculated to be 11.3 Å. This calculated value is in excellent agreement with the value determined from the experimental work of Jones. It must be remembered that it depends upon the compensation effect ($k_1 = k_2$) in the calculation of the ratio of the frequencies of collision of the two salts and also upon a result obtained from an arbitrarily extrapolated curve. The first of these assumptions cannot be further tested with the data available. Similar and more extended experiments upon solutions of two completely dissociated electrolytes may settle this point.

According to the above result it may be stated that the physical meaning of the ion size parameter in the Debye–Hückel theory of solutions takes on added significance. The fact that this quantity may be used in a logical calculation of mean values is definite although indirect proof of its significance as a distance.

In conclusion we wish to acknowledge our indebtedness to the Rockefeller Foundation for financial aid which made possible the purchase of much of the equipment used in the experimental work.

Summary

A mathematical solution of the problem of the calculation of the mean distance of closest approach of the ions in dilute solutions of strong electrolytes is given. This quantity is obtained as a function of quantities depending upon the valence types of the dissolved compounds and the size of the individual ions.

The activity coefficients of lead chloride in solutions of cadmium nitrate have been determined at six concentrations. The ratio of the concentration of the lead chloride to that of the cadmium nitrate was held constant. The data obtained are used as a preliminary test of the above-mentioned theoretical calculation.

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A Comparison of Organic Inhibitors in Chain Reactions

BY KIA-KHWE JEU AND HUBERT N. ALYEA

In the oxidation of sodium sulfite inhibited by alcohols, and of benzaldehyde inhibited by anthracene, Bäckström and co-workers[1] established that the inhibitory process is accompanied by an induced oxidation of the inhibitor. This paper extends the investigation to types of reactions where such an inhibition mechanism seems improbable; for example, a polymerization carried out in a hydrogen atmosphere to the exclusion of oxygen. In place of a detailed study of products formed by one inhibitor in one reaction we have investigated the relative inhibitory effects of numerous classes of substances on several types of reactions: (1) the photo-polymerization of vinyl acetate, (2) the autoxidation of sodium sulfite, (3) the photolysis of hydrogen peroxide.

Our choice of inhibitors was limited by the necessity that they should represent as many different types of compounds as possible, were soluble in our reaction media, water or ethyl acetate, and did not absorb light in the spectral region used, 3000-4000 Å. The latter precautions eliminated any inhibition due to screening effect.[2]

Theoretical

All three reactions are chain reactions and have unimolecular velocity constants. The effect of various organic substances could, therefore, be expressed as relative inhibitory powers, k, in a velocity expression

$$\frac{dx}{dt} = k_1 (1 - x)\left[1 + \frac{k_3}{k_2 + kC}\right] \tag{1}$$

where dx is the fraction reacting in the interval dt and k_1 is the usual unimolecular constant. [1] is the primary step and $k_3/(k_2 + kC)$ is the probable number of links in a chain following the primary step. This probability is governed by k_3, the probability of continuing the chain; and $(k_2 + kC)$, the probability of breaking the chain by some constant factor, k_2, such as walls or impurities, or by the added inhibitor of concentration C.

With chains of any appreciable length the primary step in the reaction becomes negligible, and equation (1) reduces to

$$\frac{dx}{dt} = \frac{(1 - x)K}{k_2 + kC} \tag{2}$$

Integrating this we obtain

$$1/t \ln \frac{1}{1 - x} = \frac{K}{k_2 + kC} \tag{3}$$

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(1) Alyea and Bäckström, THIS JOURNAL, 51, 90 (1929): Bäckström and Beatty, *J. Phys. Chem.*, 35, 2530 (1931).

(2) Anderson and Taylor, THIS JOURNAL, 45, 650 (1923).

This equation will apply to photochemical as well as thermal reactions, provided that the reactant absorbs only a small fraction of the incident light, so that the number of chains started is proportional to $(1 - x)$. This condition is fulfilled in both the polymerization of vinyl acetate and the decomposition of hydrogen peroxide, so that equation (3) can be applied to both. The 5% vinyl acetate solutions we employed absorbed only 2% of the 3130 Å. light.[3] The 0.6 M hydrogen peroxide solutions absorbed as much as 50% of the 3132 Å. line[4] and a much smaller percentage of the 3340 and 3663 Å. lines, so that only an approximate agreement with equation (2) may be anticipated.

Experimental

Photopolymerization.—The reaction vessels and mercury lamp were immersed in a de Khotinsky thermostat at 75 ± 0.1°. A Cooper–Hewitt vertical mercury lamp was held in place inside a 2.5 X 25 cm. quartz tubing by an asbestos belt and calked with red lead-linseed oil. A small portion of the mercury reservoir projected from the bottom of the tubing, and was in direct contact with the water in the bath; the amount projecting was so adjusted that the lamp burned at 180 watts. The quartz tube was cemented in a brass collar in the center of a brass rack and tripod. On the periphery of the rack, and equidistant from the mercury lamp, eight holes were bored to accommodate eight Pyrex reaction vessels. Each vessel consisted of two parts: an outer tube 19 cm. long, the lower part 9 X 2 cm., the upper part 10 X 1.5 cm.; and an inner tube of 6 mm. o. d. tubing 37 cm. long with a stopcock 10 cm. from the upper end, below which was an enlargement ground to fit into the outer tube. The lower end was tapered and reached within 0.5 cm. of the bottom of the outer tube, whose contents were thereby well mixed and the gas space thoroughly flushed with hydrogen. The 16-cc. samples used in a run were completely exposed to the rays from the mercury lamp.

Pure vinyl acetate was supplied by the Union Carbide and Carbon Company and c. P. ethyl acetate by Merck and Company. They were simultaneously distilled in a hydrogen atmosphere in separate flasks on a water-bath at 80°. From the moment the distillation was begun to the time when all solutions were mixed and the polymerization measurements commenced, all operations were carried out in an atmosphere of tank hydrogen, to the complete exclusion of air.

8.45 cc. of the middle portion of the vinyl acetate distillate was diluted with 150 cc. of ethyl acetate; 15 cc. of this was mixed in a reaction vessel, with 1 cc. of inhibitor solution. Eight reaction tubes were filled in the same way and placed in the bath at the same time. Two always served as blanks aad contained 1 cc. of ethyl acetate instead of 1 cc. of inhibitor solution. The ground joints were lubricated with completely polymerized vinyl acetate dissolved in ethyl acetate

Merck c. P. or other products of equal quality were used without further purification in preparing the inhibitor solutions in 25.00-cc. lots by dissolving 0.02148 mole of inhibitor in ethyl acetate. This gave a concentration in the reaction vessel of one inhibitor to ten of vinyl acetate molecules. More dilute inhibitor concentrations were prepared by dilution of the 25-cc. lot. The initial vinyl acetate concentration was always 5% (0.536 molar).

At convenient time intervals during a polymerization run two 2-cc. samples were removed and their iodine values determined: 10 cc. of carbon tetrachloride, 2 cc. of un-

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(3) Taylor and Vernon, THIS JOURNAL, 63, 2637 (1931).

(4) Kornfeld, Z. Phot., 21, 66 (1922).

known, and 25 cc. of Wijs solution were allowed to stand in a glass-stoppered 500-cc. bottle for thirty minutes in the dark. Then 10 cc. of 10% potassium iodide solution and 200 cc. of water were added, and the iodide liberated by the remaining Wijs solution titrated at once with $N/10$ thiosulfate solution, starch emulsion being added toward the end.[5]

Wijs solution was prepared by bubbling chlorine gas through 13 g. of Merck resublimed iodine dissolved in one liter of glacial acetic acid until the halogen content was doubled.[6] The acetic acid should not contain reducing substances nor over 0.5% of water, since both affect the keeping quality of Wijs solution.

Autoxibation.—The apparatus and procedure for the thermal oxidation of sodium sulfite was identical with that used by Alyea and Bäckström,[1] except that ordinary distilled water and Merck C. P. anhydrous sodium sulfite were used without further purification. Decrease in sulfite concentration was followed by titration with 0.5 N sulfuric acid to PH 4.3, using brom cresol green as indicator. Since the titration consists in changing SO_3^{--} to HSO_3^-, 5 cc. of 0.6 M sulfite requires 6 cc. of 0.5 N sulfuric acid. Standard aqueous inhibitor solutions were prepared containing 0.012 mole of inhibitor in 50 cc. of solution; 5 cc. of this added to 15 cc. of 0.8 M sulfite buffered with sulfuric acid gave a concentration of one inhibitor to ten sodium sulfite molecules. The initial sulfite concentration was always 0.6 molar.

Photolysis.—The apparatus was the same as in the photopolymerization except that the inner tube was replaced by a loosely fitting stopper. A stock solution of 50 cc. of Merck Superoxol diluted with 450 cc. of distilled water was used to prepare 0.8 molar hydrogen peroxide. For each run 15 cc. of the latter was mixed with 5 cc. of the aqueous inhibitor solutions described above. Two 1-cc. samples were removed from time to time during the run, and the peroxide content determined by titration with $N/10$ potassium permanganate in the usual way. The experiments were made at 75°, the initial peroxide concentration being 0.6 molar.

Results

Wijs Method for Following Polymerizations.—Not more than half of the Wijs solution should be consumed by the vinyl acetate, so that not more than 2 cc. of a 5% solution of vinyl acetate should be used in the directions above. Thus, with 5% solutions we obtained upon titrating 2-cc. samples an experimental iodine number of 294.2; with 4-cc. samples, 266.9. The theoretical iodine number is 294.9, showing that there was incomplete addition with the 4-cc. samples. Ethyl acetate does not react with Wijs solution; nor does the polymerized product, since sections cut from some solid photopolymerized vinyl acetate gave iodine values as low as 9.5 and 6.3, corresponding to 96 and 98% polymerized. In a few cases a blank titration and correction had to be applied for a small amount of Wijs solution reacting with the inhibitor. Wijs solution is rapid in action and keeps for months. It surpasses other methods which have been used in following the polymerization, especially since it is applicable to very dilute solutions. This, aside from obviating experimental difficulties of working with very viscous solutions, evades the danger of association in solutions

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(5) Kolthoff and Furman, "Volumetric Analysis," Vol. I, p. 198; Buckwalter and Wagner, THIS JOURNAL, 52, 5241 (1930); Böeseken and Gelber, *Rec. trav.* chim., 46, 158 (1927).

(6) Sherman, "Methods of Organic Analysis," 2d ed., The Macmillan Co., New York, 1929, p. 152.

which according to Staudinger and Heuer[7] occurs in these solutions whenever the concentration exceeds a few per cent.

Confirmation of the Velocity Equation.—In all three reactions x is the fraction which has reacted after t hours. C is the ratio of the number of inhibitor to number of reactant molecules. Equation (3) may be written

$$\frac{k_2}{t}\ln\frac{1}{1-x} + \frac{kC}{t}\ln\frac{1}{1-x} = K \tag{4}$$

For the photo-polymerization the wattage of the mercury lamp although constant throughout a single run varied between 170 and 200 watts from day to day. This necessitated a correction w the value of which was determined empirically by dividing the value of $x/2-x$ at the wattage used during the experiment by the value of $x/2-x$ at 180 watts, the latter wattage being taken as standard. This introduced into equation (4), in which the expanded form $2x/2-x$ is used in place of $\ln 1/1-x$, gives

$$\frac{Kwt}{(kwt/2)+k_2+kC} \tag{5}$$

That this equation is satisfied over a large range of concentrations is shown for pyrogallol, hydroquinone and benzylamine in Tables I, II and III and in Fig. 1.

TABLE I

POLYMERIZATION INHIBITED BY PYROGALLOL

$k = 3200$; $w = 0.92$; $t = 3$ hours

$1/C$	KC	x Calcd. $\left(= \frac{0.22\,wt.}{0.11\,wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.378	0.380
5000	0.64	.270	.273
2500	1.28	.210	.176
1000	3.20	.126	.130
500	6.40	.076	.070
100	32	.018	.027
50	64	.009	.017
10	320	.002	.015

TABLE II

POLYMERIZATION INHIBITED BY BENZYLAMINE

$k = 130$; $w = 1.0$; $t = 3$ hours

$1/C$	kC	x Calcd. $\left(= \frac{0.22\,wt}{0.11\,wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.405	0.403
5000	.026	.399	.390
2500	.052	.392	.420
1000	.13	.375	.393
500	.26	.349	.349
100	1.3	.225	.235
50	2.6	.156	.158

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(7) Staudinger and Heuer, *Ber.*, 62, 2933 (1929).

TABLE III

POLYMERIZATION INHIBITED BY HYDROQUINONE

$k = 1000$; $w = 0.86$; $t = 3$ hours

$1/C$	kC	x Calcd. $\left(= \frac{0.22\,wt}{0.11\,wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.358	0.362
2500	0.4	.286	.294
1000	1.0	.219	.222
500	2.0	.158	.159
100	10.0	.049	.059
50	20.0	.026	.063
10	100.0	.006	.008

For the oxidation of sodium sulfite, if the reaction is followed over small changes in x, the value of $1 - x$ in equation (2) remains essentially constant, and the equation reduces to that already shown by Backstrom[8] to be approximated in inhibited sulfite oxidation.

For inhibited photolysis, a thermal run was made in each case and deducted from the observed light rate to give the true photochemical rate. The uninhibited thermal rate was only 7% of the photochemical one. At a concentration of 1/500 all of the substances inhibited the normal thermal reaction with the exception of ethylamine. The latter accelerated[2] roughly in proportion to its concentration: 14-fold at 1/100, 4-fold at 1/500 and 1.2-fold at 1/2500. However, at no time did the thermal rate exceed the photochemical one, and with most inhibitors it was around 10% of the photochemical rate. At a concentration of one-tenth the thermolysis was accelerated 5-fold by pyrogallol, 4-fold by resorcinol, and 2.5-fold by hydroquinone, possibly due to reaction with the peroxide; so that this concentration was not used in evaluating their inhibitor powers. That a unimolecular equation is obeyed in the

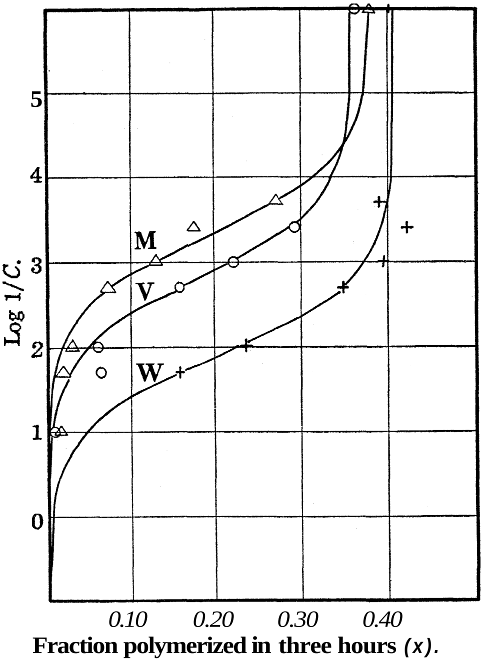

Fig. 1.—M, Pyrogallol (W = 0.92); V, hydroquinone (W = 0.86); W, benzylamine (W = 1.00). △ ○ + values observed; —— values calculated from $x = 0.22\,wt/(0.11\,wt + 1.30 + kC)$.

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[8] Bäckström, THIS JOURNAL, **49**, 1460 (1927).

photochemical decomposition of pure or inhibited hydrogen peroxide at 75° is shown in Tables IV and V.

TABLE IV

PHOTOLYSIS OF HYDROGEN PEROXIDE IN UNINHIBITED SOLUTIONS AT 75°

t in hours	Photothermal	Thermal alone	Photo alone x	$1/t \log 1/(1 - x)$
0.0	0.000	0.000	0.000	
0.6	.490	.028	.462	0.450
0.9	.678	.037	.641	.500
1.2	.800	.045	.755	.517
1.5	.880	.052	.828	.475
2.0	.945	.061	.884	.470
				Av. 0.482

TABLE V

PHOTOLYSIS OF HYDROGEN PEROXIDE INHIBITED BY VERONAL AT 75°

$1/C$	t in hours	Photothermal	Thermal alone	Photo alone x	$1/t \log 1/(1 - x)$
100	0.3	0.137	0.007	0.130	0.223
100	.6	.262	.014	.248	.207
100	.9	.359	.022	.337	.196
500	.3	.222	.013	.209	.430
500	.6	.411	.027	.384	.352
500	.7	.507	.036	.471	.350
2500	.3	.261	.021	.240	.400
2500	.6	.486	.044	.442	.426
2500	.8	.602	.058	.058	.432

Evaluating the Relative Inhibitor Power k.—It is only possible to give k, k_2 and K in equation (4) numerical values by assigning one of them a definite value for some standard inhibitor. Experimentally, the results with powerful inhibitors were found to be most reproducible; of which pyrogallol was chosen as the standard, and assigned a k-value of 3200 for all three reactions. This number was chosen because ethyl alcohol, one of the weakest inhibitors known, was found thereby to assume a value of approximately unity. All substances, therefore, excepting those whose inhibitory powers were immeasurably small, have a value of k greater than unity.

For the *polymerization* of vinyl acetate, when $kC/t \ln 1/1 - x$ is plotted against $1/t \ln 1/1 - x$ for pyrogallol, all of the values fall along the same line, as shown in curve 1, Fig. 2. This conforms with equation (4) which indicates that when C approaches infinity $C/t \ln 1/1 - x = K$, and that when C is zero $k_2 = K/(1/t \ln 1/1 - x)$. Reading these values from the intercepts at the axes we obtain

$$K = 0.22 \text{ and } k_2 = 0.22/0.170 = 1.30$$

This method is extended to the other inhibitors by graphing $C/t \ln 1/1 - x$ against $1/t \ln 1/1 - x$ and then multiplying the ordinate values by some constant, k, which brings the intercept at the ordinate up to 0.22. Examples are shown in Curve 1, Fig. 2, for hydroquinone and benzylamine.

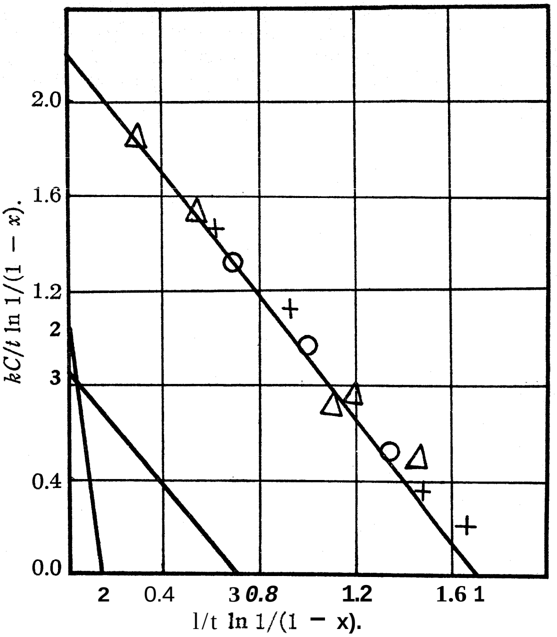

Fig. 2.—General curves for all inhibitors: Curve 1, photo-polymerization of vinyl acetate, 5% solution, in which the scale is increased ten-fold, the observed intercepts being 0.17 and 0.22; △ pyrogallol, ○ hydroquinone, + benzylamine; Curve 2, thermal autoxidation of sodium sulfite, 0.6 molar; Curve 3, photolysis of hydrogen peroxide, 0.6 molar.

The relative inhibitor powers so determined are given in Table VI and have been obtained from at least ten runs on each inhibitor. The intercept at the abscissa, which corresponds to the uninhibited rate, was strictly reproducible.

For the oxidation of sodium sulfite corrections must be applied. Unless there is extreme purification of the sulfite long induction periods are obtained. This difficulty is obviated by referring each run to exactly the same amount oxidized, a drop in sulfite concentration from 0.60 to 0.46 molar being taken as the standard. When this is done all experimental points for any given inhibitor lie along the same line when $C/t \ln 1/1 - x$ is plotted against $1/t \ln 1/1 - x$. The intercepts at the axes for these graphs are given in Table VII. It will be noticed that the intercept at the abscissa is not strictly reproducible, due to varying impurities in the sulfite. This was corrected for by assigning a standard value, 0.15, at the abscissa

TABLE VI

RELATIVE POWERS OF INHIBITORS IN VINYL ACETATE PHOTOPOLYMERIZATION

Inhibitor	Inhibitor constant k	Inhibitor	Inhibitor constant k
Benzene	2.3	Methyl oxalate	1.2
Ethyl alcohol	1.2	Ethylamine	45
Allyl alcohol	58	Benzylamine	130 ± 5
Benzyl alcohol	26		
Chloral hydrate	0.0	Phenol	16
		Hydroquinone	1000 ± 20
Propionic acids	0.0	Pyrocatechol	1400 ± 70
Benzoic acid	5.8	Resorcinol	29
		Pyrogallol[a]	3200 ± 175
Pyridine	12.0		

[a] This number taken as standard. The observed intercept at the abscissa for all curves is 0.170. The observed value for $C/t \ln 1/(1-x)$ at the intercept at the ordinate for each curve is $0.22/k$.

TABLE VII

RELATIVE POWERS OF INHIBITORS IN SULFITE OXIDATION

(No copper sulfate added)

Inhibitor	1/concentration range of inhibitor (1/C)	Intercepts		Ordinate'	Inhibitory power k
		Observed Absc.	Corrected Ord.		
Propionic acid	10-100	...	.....	.....	Accelerates slightly
Methyl oxalate	20-100	0.378	w	.....	0.0
Benzoic acid	100-1000	.168	∞	.....	.0
Cocaine hydrochloride	500-1000	.120	∞	.....	.0
o-Cresol	20-500	.175	∞	.....	.0
Ethyl alcohol	0.5-50	.132	1.0000	1.130	.9
Chloral hydrate	10-500	.280	0.4360	0.2340	5
Phenol	10-500	.168	.0580	.0518	20
Acetoxime	10-500	.190	.0475	.0375	28
Resorcinol	5-500	.350	.0810	.0348	30
Acetamide	10-50	.135	.0300	.0333	32
Veronal	100-500	.320	.0710	.0333	32
Benzyl alcohol	10-100	.100	.0210	.0314	34
Pyridine	10-100	.156	.0200	.0192	55
Ethylamine	5-100	.200	.0140	.0105	100
Allyl alcohol	10-100	.290	.0185	.00955	110
Benzylamine	10-500	.330	.00648	.00295	360
Pyrocatechol	50-100	.0348	.000582	.....	1800
Pyrogallol	50-100	.055	.00033	.....	3200[b]
	500-2500	.140	.00076	.000082	(13000)
Hydroquinone	50-500	.0348	.000118	.....	9000
	1000-5000	.145	.000043	.000045	(24000)

[a] Corrected intercept at abscissa is 0.150 for all but the last three inhibitors. [b] This number taken as standard.

for the blank rate, $C = 0$, and correcting all curves to this standard so as to be comparable. The general curve is given in Fig. 2, Curve 2. It will be noticed also that the last three inhibitors at concentrations greater than 1/500 cut the abscissa at abnormally low values. For these the observed intercepts at the ordinate were used without correction. The values for k obtained from at least ten runs on each inhibitor are given in Table VII.

TABLE VIII

RELATIVE POWERS OF INHIBITORS IN SULFITE OXIDATION

(Accelerated by 5 X 10^{-6} molar $CuSO_4$)

Inhibitor	1/concn. range of inhibitor 1/C	Intercepts Observed Absc.	Ord.	Corrected ordinate	Inhibitory power k	
Ethyl alcohol	0.5–1000	0.224	1.5000	1.0000	1.6	(0.9)[b]
Phenol	10–500	.263	0.1230	0.0704	23	(20)
Resorcinol	10–500	.250	.0970	.0582	27	(30)
Benzyl alcohol	10–1000	.230	.0815	.0532	30	(34)
Pyrocatechol	50–500	.110	.00097	....	1600	(1800)
	1000–5000	.250	.000204	.00012	3000	....
Pyrogallol	50–500	.063	.00050	....	3200	3200[c]
Hydroquinone	500-5000	.265	1.00010	.00058	28000	(24000)

[a] Corrected intercept at abscissa is 0.15 for all inhibitors.

[b] Values in absence of copper sulfate, taken from Table VII.

[c] This number taken as standard.

TABLE IX

RELATIVE POWERS OF INHIBITORS IN HYDROGEN PEROXIDE PHOTOLYSIS

Inhibitor	1/concn. of inhibitor 1/C	Intercepts Observed Absc.	Ord.	Corrected ordinate"	Inhibitory power k
Ethyl alcohol	10–20	0.732	0.0622	0.0598	130
Allyl alcohol	10–500	.672	.0525	.0550	150
Propionic acid	50–500	.770	.0143	.0131	640
Chloral hydrate	100–500	.460	.00690	.0106	790
Pyridine	10–500	.623	.00705	.00796	1040
Acetoxime	10–500	.802	.00875	.00770	1080
Veronal	100–2500	.985	.00945	.00678	1230
Methyl oxalate	50–100	.484	.00286	.00416	2000
Pyrogallol	100–2500	.825	.00304	.00260	3200[b]
p-Cresol	100–500	.664	.00140	.00149	5600
Benzyl alcohol	10–500	.705	.00124	.00124	6700
Pyrocatechol	100–2500	.691	.00099	.00101	8200
Hydroquinone	100–2500	.770	.00108	.00079	8400
Benzoic acid	500–2500	.904	.00109	.00085	9800
Resorcinol	500–1000	.691	.00076	.000775	11000
Phenol	500–1000	.737	.00077	.000737	11000
Cocaine hydrochloride	500	.705	.000691	.000691	12000
Benzylamine	500–2500	.857	.000815	.000671	12000
Ethylamine	500–2500	.830	.000488	.000410	20000

[a] The corrected intercept at the abscissa is 0.705 for all inhibitors. [b] This number taken as standard.

Some runs were also made on sodium sulfite solutions accelerated by 5×10^{-6} molar copper sulfate. The inhibitory powers for these solutions as given in Table VIII agree with the values in unaccelerated solutions.

For the *photolysis* of hydrogen peroxide there was no induction period, but a blank rate with a value of $l/t \ln 1/(1 - x) = 0.705$ was assigned (see Table IX, Curve 3, Fig. 2).

Photosensitization of Polymerization.—Taylor and Vernon[3] found that the quantum yield for vinyl acetate polymerization is unity at 2300 Å. and 2536 Å. but 1000 between 30004000 Å. The low value might be due to depolymerization occurring simultaneously and thereby masking the true polymerization rate; or to the light being absorbed by a photochemically inactive portion of the molecule, an "intra-molecular screening effect," analogous to the effective decrease in quantum yield with wave length in the decomposition of acetaldehyde.[9] A search was therefore made for photosensitizers to higher wave lengths at which these retarding effects might be nil. No attempt was made to weigh accurately the added sensitizer, our only intent being to discover one which gave a many-fold increase in rate. Semi-quantitative measurements in which the ratio of proposed sensitizer to reactant molecules ranged from 1:1 to 1:10 for liquids, and 1:20 to 1:10,000 for solids, the latter because of extremely low solubilities of some solids, showed the following. The reaction was accelerated from five to twenty per cent. by acetone, sodium benzoate, benzoyl peroxide, chloral hydrate, phosphoric acid, fuchsine, quinine sulfate, malachite green, propionic acid, anisole, chrysaniline, phthalic acid, and alizarin-indigo blue. Without effect, were eosin, phosphine 3R and thymol. The following were weak inhibitors, which reduced the normal rate to about half: bromindigo 2B, barbituric acid, phosphine, methyl oxalate, aniline violet, ethyl alcohol, guaiacol, erythrosine B, thiophene, benzene, acetamide, benzamide *p*-rosaniline, m-cresol, benzoic acid, benzophenone, indole, alizarin red S, caffeine, pyridine, indigo bengal, phenol, cyanin, benzyl alcohol, resorcinol, rosaniline, ethylamine, neo-indol, allyl alcohol, benzil, benzylamine, acetoxime and dinitronaphthol. The following were powerful inhibitors which reduced the rate to three per cent. or less of the normal rate: picric acid, quinoline, o-nitrotoluene, dimethylaniline, aniline, furfural, diethylamine, azobenzene, rhodamine B, o-nitrophenol, salicylic acid, a-nitronaphthalene, rhodinol, nitrobenzene, allyl isothiocyanate, pyrogallol, hydroquinone and pyrocatechol.

Discussion of Results

A summary of these results and other data in Table X at once emphasizes that the relative inhibitor powers are strikingly parallel in the oxidation and polymerization reactions, and that inhibitor power in the photoly-

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[9] Kirkbride and Norrish, *Trans. Faraday Soc.*, *27*, *404* (1931).

sis, on the other hand, has nothing in common with them. Of all the inhibitors, hydroquinone alone absorbed above 3000 Å. and might well, therefore, sensitize as well as inhibit the photopolymerization; whereas such sensitization is precluded in the thermal sulfite oxidation. Therefore, k is larger in the latter. No explanation is offered for the exceptions pyridine and acetoxime, and the experimental discrepancies between Anderson and Taylor's and our values for benzoic acid and ethyl alcohol. Their value of about 20,000 was a limit of inhibitory power imposed by their experimental accuracy, and agrees well with our values when it is recalled that the concentration of their hydrogen peroxide, and, hence, the value k varied two-fold.

Let us return to the parallelism of inhibitory powers for the oxidation and polymerization. Assuming the function of the inhibitor is to receive and dissipate chain energy,[1] the relative inhibitor powers may be identical with the relative efficiencies of these twenty-odd substances in receiving excess enerpy from a "hot chain molecule." But collisions of the second kind are highly specific processes, and even though the excess energy of a hot polymerized and a hot oxidized molecule be identical, we should hardly anticipate identical collision efficiency, identical inhibitory powers. Another mechanism is possible: if the polymerization involves an initial peroxide step it may be inhibited in the same way as the peroxide stages in

TABLE X

RELATIVE POWERS OF INHIBITORS—SUMMARY

The values in columns 2, 3, 4, 7 are from this paper. Columns 5 and 6 were calculated from data in Raymond, *J. chim. phys.*, 28, 316 (1931), and Anderson and Taylor, ref. 2.

			Oxidation		Photolysis	
Inhibitor	Polymerization, vinyl acetate	Na_2SO_3, no copper	Na_2SO_3 copper accelerated	Benzaldehyde photo	H_2O_2 Anderson and Taylor	H_2O_2 Jeu and Alyea
Chloral hydrate	0	5	..	..	....	790
Propionic acid	0	0	..	..	....	640
Methyl oxalate	1.2	0	..	..	700–1400	2000
Ethyl alcohol	1.2	0.9	1.6	..	2700–5400	130
Benzoic acid	5.8	0	..	..	0–100	9800
Phenol	16	20	23	20[a]	ca 20000	11000
Benzyl alcohol	26	34	30	..	3200–6400	6700
Resorcinol	29	30	27	..	....	11000
Ethylamine	45	100	..	..	ca 20000	20000
Allyl alcohol	58	110	..	(2)	....	150
Benzylamine	130 ± 5	360	..	..	ca 20000	12000
Pyrocatechol	1400 ± 70	1800	1600	..	....	8200
Pyrogallol	3200[a]	3200[a]	3200[a]	..	....	3200[a]
Hydroquinone	1000	9000	..	2930	....	9400
Pyridine	12	55	..	..	....	1040
Acetoxime	92	28	..	..	....	1080

[a] This number taken as standard.

the sulfite oxidation. Such a mechanism might involve a competition for AO_2 by activated reactant A' molecules

$$A' + AO_2 \longrightarrow O_2 + A_2$$

subsequent rapid polymerization giving rise to A_n, or by inhibitor molecules, B

$$B + AO_2 \longrightarrow BO_2 + A$$

whereby the formation of the polymer is prevented. This of course might give identical inhibitory powers corresponding with and proportional to the oxidizability of the inhibitors by peroxides. However, the only evidence to support this view is that benzoyl peroxide accelerates the polymerization.[10] For such a mechanism an extremely small amount of oxygen may be necessary and the large excess of oxygen used by Taylor and Vernon[3] might well lead to the inhibition which they report.

k_2, a Measure of Chain Length.—Pyrogallol, our most powerful inhibitor, was assigned a standard inhibitory power of 3200. Assume that a collision of a chain molecule with pyrogallol is as efficient in breaking the chain as a collision with a reactant molecule is in continuing the chain, and accordingly assign it an absolute inhibitory power of $k_a = 1 = k/3200$. Now when pyrogallol has reduced the uninhibited rate to half, kC will equal k_2. When k_a is used in place of k, $1/C$ will be half the chain length: thus to cut a one-thousand link chain at the five hundredth link requires a concentration of 1/500 of pyrogallol to reactant molecules. That is

$$\text{chain length} = 2/(k_aC) = 6400/kC = 6400/k_2$$

If an inhibitor more efficient than pyrogallol is found, it would increase the chain length by the factor (k for new inhibitor/3200), so that the assumption that pyrogallol is 100% efficient in breaking chains gives the value of a *minimum chain length.* This calculation has been carried out in Table XI for several measurements where the value k_2 is known.

TABLE XI

CALCULATION OF CHAIN LENGTH FROM k_2

Reaction	k_2	Chain lengths calculated (= 6400/k_2)	Chain lengths probable
Polymerization of vinyl acetate 5% soln.	1.30	5000	2500
Autoxidation of sodium sulfate			
0.6 *M* Jeu and Alyea	7.04	900	1000–10000
Alyea and Bäckström	0.068	100000	100000
Backstrom	0.0059	1000000	100000
Photolysis of hydrogen peroxide 0.6 M	11.8	540 (2000)	1000

The values 1.30, 7.04, 11.8 are from this paper. Alyea and Backstrom's value[1] of $k_2 = 0.0012$, where k for benzyl alcohol was 1 and the concentration was expressed in moles of inhibitor per liter of 0.6 molar sulfite solu-

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(10) See Conant and Peterson, THIS JOURNAL, 54, 628 (1932), where a peroxide step is postulated for the polymerization of isoprene and for *n*-butyraldehyde at high pressures,

tion, gives in our units 0.0012 X 34 X 1.0/0.6 = 0.068. Bäckström's[8] value of $k_2 = 0.00906$, where k for benzyl alcohol was 60 and concentration was expressed in moles per liter of 0.6 molar sulfite solution, gives in our units 0.00622 X 34/60 X 1/0.6 = 0.0059. The value 2500 in the last column is a semi-quantitative quantum yield which we obtained by comparing the polymerization rate and light absorption of a 100% vinyl acetate solution for which Taylor and Vernon[5] obtained a quantum yield 1000, with the values for a 5% solution. The sulfite we used was not purified and exhibited long induction periods, and undoubtedly the chains were ten to a hundred-fold shorter than in Alyea and Backstrom's sulfite, for which they found chain lengths of 100,000, by induced oxidation of alcohols. Chains of 500 for hydrogen peroxide have been experimentally measured by Allmand and Style[11] and they postulated that they are considerably longer than this. A value 540 is obtained with 3200 for pyrogallol, but using a k of 12,000, which the more powerful amines and phenols possess, gives a minimum chain length of 2000 at 75°. The agreement is all that could be desired except in the case of Backstrom's sulfite measurements, in which different samples of sulfite used in the inhibited reaction and in the photochemical reaction, or even different reaction vessels, are sufficient to cause a several-fold change in reaction rate.

Summary

1. Photopolymerization of vinyl acetate may be followed by determining iodine numbers with Wijs solution.

2. A general equation $\frac{1}{t}\ln\frac{1}{1-x} = \frac{K}{k_2 + kC}$ represents the behavior for chain reactions of the first order in the presence of inhibitors. x is the fraction reacting during time t, K is composite of the number of chains initiated at t = 0 and the probability of continuing the chains; while $k_2 + kC$ is the probability of breaking the chains by a constant factor k_2 or by an inhibitor of concentration C and inhibitor power k.

3. The equation represents the photopolymerization of vinyl acetate, the thermal autoxidation of sodium sulfite and the photolysis of hydrogen peroxide.

4. Among sixteen representative inhibitors which include alcohols, esters, acids, amines, oximes, phenols, aldehydes, and alkaloids, the relative inhibitor power for a given substance is approximately identical in the polymerization of vinyl acetate and oxidation of sodium sulfite. In the photolysis of hydrogen peroxide, however, the values of k have no obvious relation to those in the other two reactions.

5. A maximum of twenty per cent. photosensitization to visible light was found for the polymerization among seventy organic substances tried.

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(11) *Allmand and* Style, *J. Chem. Soc.*, 596 and 606 (1930).

6. Chain lengths agreeing with experimental values may be predicted from the values of k_2.

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The Photochemical Reaction between Quinine and Dichromic Acid. II. Kinetics of the Reaction

BY GEORGE S. FORBES, LAWRENCE J. HEIDT AND F. PARKHURST BRACKETT, JR.

This paper suggests a kinetic picture consistent with new data and with data already published.[1] The experimental methods have been described[1] except those followed (by the last-named author) at 208, and 254 mμ.

The only primary act (except possibly at 208 mμ) contributing to reduction of dichromic acid disclosed by our results is an activation of the quinine molecule or ion, Q to form Q*. In the secondary act a part of these activated molecules reduces dichromic acid. This picture could be amplified as follows. At the instant of excitation Q may be adjacent to molecules (or ions) of the other reactants, all within possibly effective ranges of distances and of orientations. That is, $n_1[Q] + n_2[H_2Cr_2O_7] + n_3[H^+] \rightleftharpoons$ potentially effective kinetic "clusters," to borrow Weigert's general designation.[2] Such clusters are conditioned by kinetic and electrostatic effects, and are in no sense stable complexes like uranyl oxalate. Photochemical reactivity, while varying with configuration, is practically independent of all activation energies except that of Q*. In a steady state and in a thin layer,

$$K_1\phi_q = [Q^*]_{\text{cluster}}/[Q^*]_{\text{total}} = K_2[Q^*]^{n_1}[H_2Cr_2O_7]^{n_2}[H^+]^{n_3}/[Q^*]$$

or

$$\log \phi_q + \log K_1/K_2 = (n_1 - 1)\log [Q^*] + n_2 \log [H_2Cr_2O_7] + n_3 \log [H^+]$$

where ϕ_q is net quantum yield referred to light absorbed by quinine and $[Q^*] = K'[Q]$ where K' depends, among other factors, upon the reaction cell used. K_1 is itself complex, involving factors such as $K_3e^{-\theta d/\theta_0 d_0}$ where θ_0 and d_0 indicate orientation and distance optimal for the secondary act.

If $[H_2Cr_2O_7]$ and $[H^+]$ are large compared with [Q], or are held constant, $\log \phi_q = (n_1 - 1) \log [Q] + \text{const.}$ For correct evaluation of n_1, deviations from the reciprocity law had to be avoided by stopping down the front lens of the monochromator in each experiment to such an extent that the quinine in the first centimeter of the reaction mixture absorbed just as many quanta per minute, E_q, as in any other experiment in the series. As a consequence, $[Q^*]_{av.}$ was always the same in the layer thus

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(1) Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).
(2) Weigert, *Z. physik.* Chem., **102**, 416 (1922); 106, 426 (1923).

defined, also in other layers uniformly defined. Table I gives the data for one typical series of experiments. E_0 equals quanta per minute incident upon the cell.

TABLE I

λ, 366 mμ. **Temperature,** 5°

$[K_2Cr_2O_7]$	$[H_2SO_4]$	[Q]	E_0	E_q	ϕ_q
0 00016	0.8	0.000250	$6\ 4 \times 10^{16}$	4.9×10^{16}	0.057
00016	.8	.000025	19.2×10^{16}	4.5×10^{16}	.059
.00016	.8	.000010	47.0×10^{16}	4.8×10^{16}	.057

Table I proves that ϕ_q when properly determined is independent of [Q]. Therefore $(n_1-1) = 0$ and $n_1 = 1$; that is, only one molecule of Q is involved in the secondary act. Similar data plotted at 405 and **313** mμ previously given,' and in Fig. 1 obtained at 366, 280, 254 and 208 mμ, lead to identical conclusions.

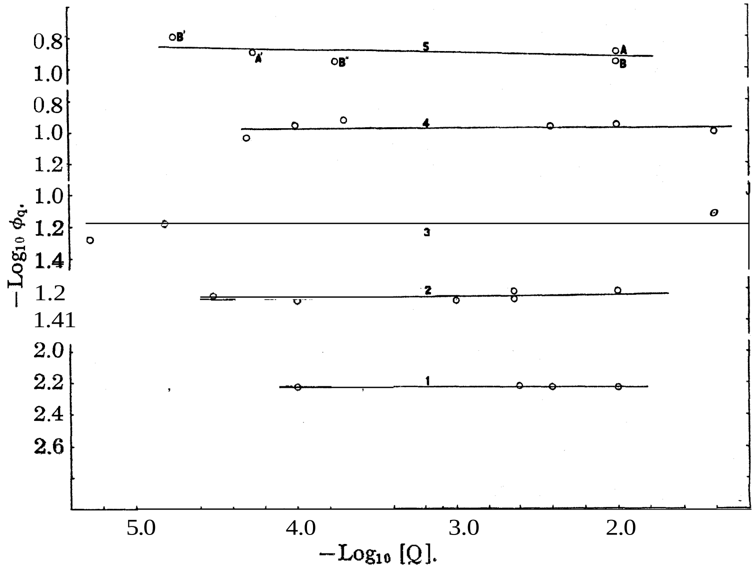

Fig. 1.—$[K_2Cr_2O_7]$, 0 00016; Temp., 23°; E_q, 5×10^{16}.

Curve	λ in mμ	$[H_2SO_4]$	Slope, n_1
1	366	0.0	0.00
2	366	.8	.00
3	254	.8	.02
4	280	.8	.00
5	208	.8	−.02
		Average	.00

At 254 and 208 mμ a zinc spark consuming 3 k. w. and automatically kept constant over long periods was used as a source of light.[3] Details of

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[3] Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

the crystal quartz monochromator working at f2 and its operation will be somewhat amplified elsewhere. Quantum yields and absorption coefficients were measured in a rectangular quartz cell (all seams fused) 85 mm. high, 35 mm. wide and 5.7 mm. thick, placed between the exit slit and the thermopile by which the highly divergent beam was integrated. The method, precautions and corrections followed closely previous investigations in this Laboratory.[4] At these wave lengths all experimental difficulties were increased, also the radiometric corrections, made as previously described. ϕ_q is given after correction for direct photolysis of dichromic acid absorbing E_c quanta per minute. The need for such a correction appears in Table II.

TABLE II

Temperature, 25". E_c, 5 X 10^{16}

λ	$[K_2Cr_2O_7]$	$[H_2SO_4]$	ϕ
208 mμ	0.00016	0.8	0.012
208	,00032	.8	.013
254	.00016	.8	.004
254	.00036	.8	.005
280	.003	.8	.000

In Fig. 1 at 254 mμ the curve appears nearly horizontal, as was the case at 280,313,366 and 405 mμ. At 208 mμ, however, the points B', A' and B", as [Q] approaches zero, suggest that the curve may be turning upward as dichromic acid absorbs a greater share of the light. Points A and A', which average a preliminary set of experiments, should be given less weight than the others. Points B and B', on the other hand, each average three very concordant final experiments. It, therefore, appears possible that at 208 mμ we have two activated reactants, each one reacting to a measurable extent with the other in its normal state. Conclusive evidence upon this admittedly important point would require a further refinement of experimentation, hard indeed to attain. Clusters in which both reactants are simultaneously activated[6] might well be exceedingly reactive, but an event of such a type ought to be so infrequent as to contribute negligibly to the total reaction.

The data graphed in curve 1, Fig. 1, at 366 mμ were collected to test Morton's prediction[6] that the efficiency of dichromic acid as an oxidant of quinine should increase, with increase of $[H_2SO_4]$ from zero to 0.37, to a maximum incapable of still further increase through light absorption. In the series, E_q was held constant as described above and no sulfuric acid was added, the quinine bisulfate and dichromic acid being so dilute no precipitate appeared. As in the other curves in the figure, ϕ_q is unchanged even at minimal values of [Q] where the greater part of the

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(4) (a) Villars, THIS JOURNAL, 49, 362 (1927); (b) P. A. Leighton and G. S. Forbes, *ibid.*, 61, 3549 (1929); (c) W. G. Leighton and G. S Forbes, *ibid.*, 52, 3139 (1930).

(5) Compare paper of Forbes, Woodhouse and Dean. *ibid.*, 45, 1891 (1923).

6) Morton, J. Phys. *Chem.*, 33, 1135 (1929).

light available is absorbed by dichromic acid. As ϕ_q does not even now increase when [Q] becomes very small, it is evident that at minimal acidity light has not measurably increased the reactivity of dichromic acid toward non-illuminated quinine.

Table III presents typical data for evaluation of n_2.

TABLE III

λ, 280 mμ. *Temperature, 25°*

[Q]	$[H_2SO_4]$	$[K_2Cr_2O_7]$	E_0	E_q	ϕ_q
0.001	0.8	0.00016	2.17×10^{16}	1.26×10^{16}	0.094
.001	.8	.00008	1.71×10^{16}	1.30×10^{16}	.069
.001	.8	.00004	1.50×10^{16}	1.30×10^{16}	.048

Similar series completed at 405, 366 and 280 mμ are shown in Fig. 2, where log ϕ_q is plotted against log $[K_2Cr_2O_7]$ at various wave lengths and temperatures. The black dots are based upon Table VIII of Luther and

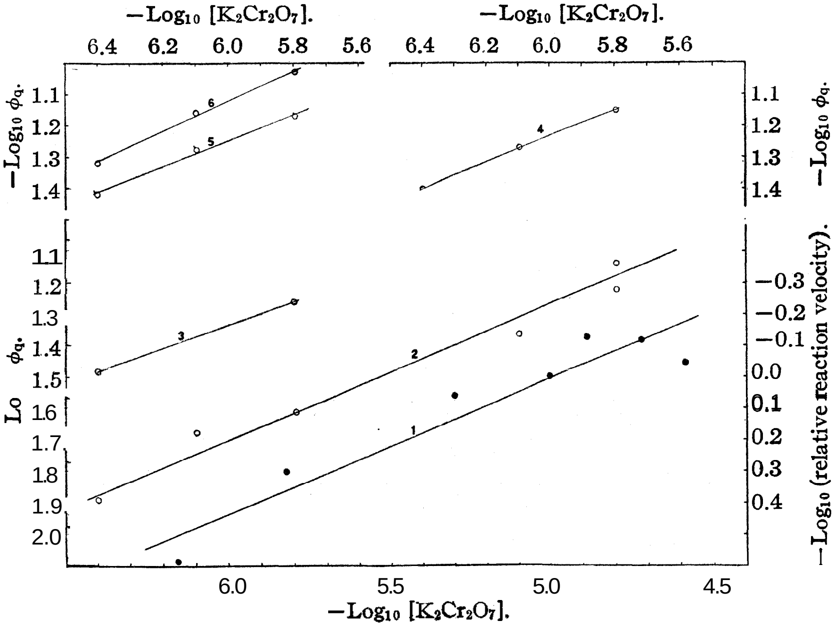

Fig. 2.—⊙, Temp. 23°; -○, Temp. 5°; ●, Data of L. & F., Ref. 7; $[H_2SO_4]$, 0.8; E_q, 5×10^{16}.

Curve	λ in mμ	[Q]	Slope, n_2
1	405	0.01	0.43
2	405	.004	.43
3	313	.00025	.38
4	366	.00025	.40
5	280	.001	.41
6	280	.001	.48
		Average	.42

Forbes,[7] log of the relative reaction rates in polychromatic light, 405 and 366 mμ, being plotted as ordinates in place of log ϕ_q. It is noteworthy that straight lines result in all cases, log $\phi_q = n_2 \log[H_2Cr_2O_7] + \text{const.}$; n_2 is uniformly **0.43 ± 0.05** irrespective of wave length or temperature, which assigns only half the molecule $H_2Cr_2O_7$ to an effective cluster. Possibly chromic acid reacts more readily with Q* than dichromic acid. Since $[H_2CrO_4] = k[H_2Cr_2O_7]^{1/2}$, a plot of log ϕ_q against log $[H_2Cr_2O_7]^{1/2}$ would have a slope equal to unity within the experimental error and would represent the behavior of clusters containing one molecule of chromic acid. The residue of the chromate molecule, bereft of one oxygen atom, is unstable and would be expected to react again, doubling the immediate quantum yield.

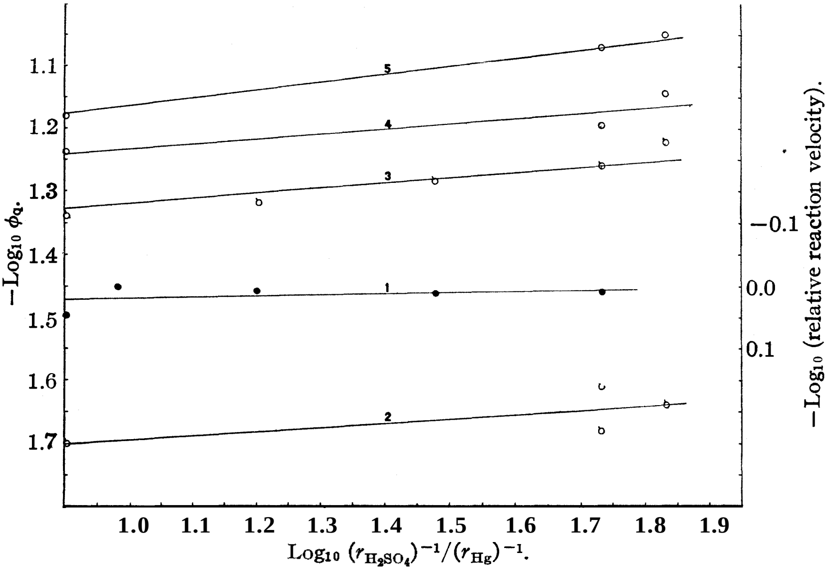

Fig. 3.—○, Temp. 23°; -○, Temp. 5°; ●, Data of F. W. & D.. Ref. 5; $[K_2Cr_2O_7]$, 0.00016; E_q, 5 × 10^{16}.

Curve	λ in mμ	[Q]	Slope, n_3
1	405	0.006	0.02
2	405	.008	.06
3	366	.00025	.08
4	313	.00025	.08
5	280	.001	.13
		Average	.07

The evaluation of n_3, for hydrogen ion, was hampered by lack of data on activity coefficients in rather concentrated sulfuric acid. Specific conductivity, r^{-1}, is perhaps the next best measure of the activity of hydrogen ion in clusters. In Fig. 3 log ϕ_q is plotted against $\log[(r_{H_2SO_4})^{-1}/$-

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[7] Luther and Forbes, This Journal, 31, 770 (1909).

$(r_{Hg})^{-1}$], taken from Kohlrausch's tables.[8] The data of Forbes, Woodhouse and Dean[5] appear as black dots, log of the relative reaction rates in polychromatic light being plotted as ordinates in place of ϕ_q. Straight lines again result, but the average slopes assign to n_3 the value 0.07 and to sulfuric acid a subordinate role in the reaction. Possibly the hydrogen ion already present in $H_2Cr_2O_7$ or H_2CrO_4 usually suffices for the secondary act involving Q*, the additional hydrogen ion in the cluster increasing only slightly the probability of the same.

The data on the reciprocity law, before plotting,[9] were subjected to a correction not discussed at that time, the need for which appears in Table IV.

TABLE IV

λ, 366 mμ. Temperature, 22°

	[Q]	[$K_2Cr_2O_7$]	[H_2SO_4]	$E_q \times 10^{-16}$	Minutes irradiated	Total min. before titration	ϕ_q, uncorrected
1	0.00025	0.00016	0.8	8	60	75	0.062
2	.00025	.00016	.8	8	60	1260	.077
3	.00025	.00016	8	8	120	135	.065

As solution (2) was exposed for the same time as (1), the difference in ϕ_q is attributable to a *dark* reaction between the photochemical oxidation products and dichromic acid during twenty-one hours as the values of ϕ_q in Table IV were corrected for the dark reaction not involving photochemical oxidation products of quinine. Experiments involving exposure to weak light over long periods are misleading until corrected for this dark reaction. Solution (3) was exposed twice as long as (1) and then titrated promptly. It is clear that the oxidation products formed during the first hour contributed little if anything to the photolysis during the second hour; that is, their quantum yield cannot greatly exceed ϕ_q. A fourth solution was photolyzed (λ, 366 mμ) until about half the quinine was oxidized. Absorption of 3×10^{20} quanta (λ, 436 mμ) by the dichromic acid in the solution followed without any effect, proving that the photochemical oxidation products, like quinine, are not photochemically oxidized in blue light.

The corrected decrease in ϕ_q with increase in light intensity,[9] as well as the small size of ϕ_q itself, suggests the hypothesis that photochemically efficient clusters are formed at a relatively slow rate. An increased light intensity might be expected to eliminate such clusters more rapidly, and cut down their concentration which existed in the previous steady state. Thereafter, a smaller fraction of the total quanta absorbed would activate quinine already present in efficient clusters, causing ϕ_q to decrease. This effect was found most striking in solutions most concentrated in dichromic acid, as shown in Table V.

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(8) Kohlrausch, "Physical Measurements," D. Appleton and Co., New York, 1874, p. 236.

(9) Ref. 1, Figs. 4, 5.

TABLE V

λ, 366 mμ. Temperature. 22°

[Q]	$[K_2Cr_2O_7]$	$[H_2SO_4]$	$E_q \times 10^{-16}$	ϕ_q
0.00025	0.00016	0.8	18.0	0.058
			1.8	.070
.00025	.00008	.8	18.0	.048
			1.8	.052
.00025	.00004	.8	18.0	.039
			1.8	.040

In a previous paper[1] the relation between wave length and quantum yield was discussed. To make the data there more complete, we have since determined ϕ_q, 0.070 at 334 mμ, compared with a value of 0.060 at 366 and at 313 mμ, under conditions otherwise identical.

Using a Judd-Lewis sector spectrophotometer in a more detailed study of the variation of the extinction coefficient of quinine, K_q, with variation of $[H_2SO_4]$ and wave length we found that from 405 to 208 mμ, log K_q is a linear function of either the log $[H_2SO_4]$ or the log [Q], the other being held constant. A shift of 200 cm.$^{-1}$ of the absorption curve of [Q], 0.0001 mole per liter, toward smaller wave numbers was observed in passing from 0.004 to 4.0 *m* H_2SO_4. In the steeper parts of the absorption curve, accurate data regarding $[H_2SO_4]$ are therefore indispensable.

Ten-degree temperature coefficients, $\delta_{10°}\phi_q = (\phi_q)_{t+10}/(\phi_q)_t$, between 5 and 24° (one determination only at 29°) at various wave lengths appear in Table VI. Each entry gives the average of two or more complete experiments. Increments of $[K_2Cr_2O_7]$ seem to lower $\delta_{10°}\phi_q$ slightly, but doubling $[H_2SO_4]$ does not seem to affect it measurably. The increase in $\delta_{10°}\phi_q$ at shorter wave lengths is too small to warrant theoretical argument. Further, the average of $\delta_{10°}\phi_q$, 1.12, approximately equals $(273 + 20)^3/(273 + 10)^3$ which suggests an interesting possibility.

TABLE VI

λ in mμ	$[K_2Cr_2O_7]$	[Q]	$[H_2SO_4]$	ϕ_q at 5 ± 1°	ϕ_q	Ten-degree temperature coefficient
366	0.00004	0.00025	0.8	0.029	0.039 at 22°	1.17
	.00004	.00025	.8	.044	.055 at 29°	1.10
	.00008	.00025	.8	.052	.054 at 23°	1.02
	.00016	.00025	.8	.062	.070 at 24°	1.07
	.00016	.00025	1.7	.060	.070 at 25°	1.08
313	.00016	.00025	0.8	.056	.064 at 24°	1.14
	.00016	.0010	.8	.052	.064 at 23°	1.16
	.00004	.00025	.8	.028	.033 at 24°	1.17
280	.00004	.001	.8	.038	.050 at 22°	1.17
	.00008	.001	.8	.054	.069 at 22°	1.16
	.00016	.001	.8	.070	.083 at 21°	1.12
404	.00016	.02	.8	.022	.028 at 22°	1.15
					Average	1.12

In a gaseous system the number of bimolecular collisions, Z, experienced by a particle having a mean free path l for a mean linear displacement $\overline{X}$ is

$$Z = 3\pi\overline{X}^2/4l^2 \qquad (1)$$

For a particle in a liquid system Einstein[10] and von Smoluchowski[11] showed that in one second

$$\overline{X}^2 = \frac{kT}{3\pi\eta r} \qquad (2)$$

where k is the gas constant per molecule, η the viscosity of the solvent, r the radius of the particle and T the absolute temperature. Granting that (1) can be made applicable to collision numbers involving ions in a liquid system by multiplying Z by a constant factor, we can substitute (2) in (1) and note that η for water between 0 and 30° is proportional to $1/T^2$, whereupon $Z = f(T^3)$. Over the temperature range 5 to 24°, $[(297)^3/(278)^3] \times 10/19 = 1.115$.

The above calculation would be also in accord with our tentative view that activated quinine reacts with dichromic (or chromic) acid in a bimolecular process requiring no additional energy of activation. It should be noted that this is not in harmony with the views held by Moelwyn-Hughes[12] and others, namely, that Z is directly proportional to the viscosity and hence has a negative temperature coefficient. If Moelwyn-Hughes' contentions are correct, a positive heat of activation, smaller than that of the average thermal reaction, would be indicated for the secondary act, and no obvious evidence of a bimolecular reaction would appear.

The investigation of quinine derivatives is being continued.

Summary

The photochemical reaction between quinine and dichromic acid apparently occurs in photochemically efficient clusters (not complexes) containing the above. Individual concentrations were varied; other variables, including concentration of activated quinine, were fixed. Seven wave lengths over the range 405 to 208 mμ were used. By graphical methods, reaction order was found to be zero for quinine and 0.43 for $H_2Cr_2O_7$ or 0.86 for H_2CrO_4. These values correspond to 0.50 and 1.00, respectively, within experimental error. A reaction order of 0.07 for H_2SO_4 assigns a subordinate role to this reactant. It is barely possible that at 208 mμ only, both the quinine and the dichromic acid are photosensitive.

It is shown that when the total absorbed light is divided between two (or more) constituents of the solution, the total intensity must be regulated so as to maintain the same concentration of the effectively activated constituent in all the experiments used to establish the effect of changing the concentration of some other reactant.

(10) Einstein, *Ann. Physik*, [4] **17**, 549 (1905); **19**, 371 (1906).

(11) Von Smoluchowski, *ibid.*, **21**, 756 (1906).

(12) Moelwyn-Hughes, *J. Chem. Soc.*, 96 (1932).

Quinine concentration being held constant, an increase in sulfuric acid concentration from 0.004 to 4 moles per liter shifts the whole absorption curve 200 cm.$^{-1}$ toward the red.

The ten-degree temperature coefficient, 1.12, agrees with one mode of calculating the temperature coefficient of the collision number in solution of a bimolecular reaction between activated quinine and H_2CrO_4 without additional energy of activation. Another calculation predicts a small energy of activation.

CAMBRIDGE, MASSACHUSETTS

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Ammines of the Lower Chlorides of Titanium

BY WALTER C. SCHUMB AND RICHARD F. SUNDSTRÖM

Although anhydrous titanium dichloride and trichloride have been the subject of numerous investigations, conflicting statements relative to some of their properties, and the absence of data concerning others, make the further study of these compounds desirable. In particular, the recorded observations which concern the preparation of the two chlorides appear in some respects to be in need of revision, and comparatively little is known concerning the reactions of these two substances with ammonia. The aim of the present paper is to contribute further information on each of these subjects.

Ruff and Neumann[1] prepared the anhydrous trichloride by reducing the tetrachloride with various metals. They obtained it as violet crystals, which when heated in a vacuum slowly began to sublime at 425°, and to decompose at 450° into the di- and tetrachlorides. At 475° this decomposition proceeded rapidly, and the dichloride thus obtained was very stable to heat and not volatile in a vacuum even at 600°. It is interesting to note that they were unable to obtain samples of high purity; they accounted for their high titanium content and low chlorine content by assuming that their samples had become oxidized during the course of the preparation. Earlier investigators similarly had failed to obtain pure specimens.

Meyer and co-workers[2] prepared the trichloride by the reduction of the tetrachloride with hydrogen at high temperatures, employing the hot-cold tube previously used by Georges and Stähler.[3] At 800–1000° they obtained a mixture of the di- and trichlorides, which was converted completely into the trichloride by heating to 300° in a stream of hydrogen and

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[1] Ruff and Neumann, Z. *anorg. allgem. Chem.*, **128**, 81 (1923).

[2] Meyer, Bauer and Schmidt, Ber., **56**, 1908 (1923)

[3] Georges and Stahler, *ibid.*, **42**, 3200 (1909).

tetrachloride vapor. Their final product, which had the appearance of violet scales, represented a yield of approximately **30%.** To account for the large proportion of dichloride in the primary product, they assumed that the reduction to trichloride was not a simple one, but rather one involving two steps

$$TiCl_4 + H_2 = TiCl_2 + 2HCl \qquad (1)$$

$$TiCl_2 + TiCl_4 = 2TiCl_3 \qquad (2)$$

The first reaction supposedly took place in the hotter parts of the reaction tube and the latter in the colder. This assumption evidently presupposes that the dichloride is volatile at high temperatures, as indeed the earlier investigators claimed. Thus Friedel and Guérin[4] reported that the dichloride volatilizes at red heat and Stähler and Bachran[5] stated that the substance sublimes at 300° in *vacuo*. In view of the fact that, according to Ruff and Neumann, the trichloride sublimes at 425°, and then but slowly, the above statements appear doubtful, since in a series of chlorides volatility, in general, decreases with decreasing chlorine content.

Experimental

Preparation of Titanium Trichloride and Titanium Dichloride.—The titanium trichloride used in this work was prepared by reduction of the tetrachloride with hydrogen at 650°. The tetrachloride previously had been distilled several times in an atmosphere of dry carbon dioxide, the colorless fraction, b. p. 136–137°, being collected in sealed tubes each containing approximately 30 g. In the reduction a modified form of the hot-cold tube described by Young and Schumb was employed.[6] In order to minimize the danger of hydrolysis during the transfer of the tetrachloride from its sealed container to the apparatus, the substance was frozen and admitted against a brisk countercurrent of dry carbon dioxide into a flask which formed part of the apparatus; thence it was slowly distilled into a second flask and the former sealed off from the latter. A stream of dry, oxygen-free hydrogen, bubbling through the liquid, carried the tetrachloride vapor into the reaction chamber (35 cm long and 30 mm. wide), which was heated in a hinged type electric furnace. The titanium trichloride formed was collected upon an 8-mm. tube, cooled internally by a rapid stream of water. The unchanged tetrachloride was recovered practically quantitatively from the effluent gas by passage through two traps, chilled to −20 and −78°, respectively.

Due to the reversibility of the reaction, $2TiCl_4 + H_2 \rightleftharpoons 2TiCl_3 + 2HCl$, in order to obtain satisfactory yields of the trichloride it is essential to remove the hydrogen chloride rapidly. Meyer and co-workers,[2] employing a gas mixture containing 16.6 mole per cent. of tetrachloride, and a reaction rate such that 20 to 30 g. of trichloride was formed in from three to four hours, accomplished this with the aid of metallic titanium present in the reaction tube. However, if a slower reaction rate was used together with a rapid hydrogen current, the concentration of hydrogen chloride could be kept low throughout the process. To this end a comparatively low reaction temperature should be used; this has the added advantage of permitting but slight decomposition of the trichloride formed. The gas mixture in the reaction chamber, moreover, should contain relatively little tetrachloride vapor; hence the liquid through which the hydrogen bubbles should be kept at a moderately low temperature. For this purpose the

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[4] Friedel and Guérin, *Compt. rend.*, **81**, 889 (1875).

[5] Stähler and Bachran, *Ber.*, **44**, 2906 (1911).

[6] Young with Schumb, THIS JOURNAL, **52**, 4233 (1930).

vapor pressure of the tetrachloride at 25° was determined and found to be approximately 21 mm. From this it may be estimated that the mixture resulting from the passage of hydrogen through the liquid at 25° contained about 2.75 mole per cent of tetrachloride vapor. The rate of flow 250 cc. of hydrogen per minute was adopted as the most suitable; under these conditions 30 g. of tetrachloride was volatilized in about nine hours. To ensure adequate drying of the gas at this rate of flow, four 60-cm drying tubes, the first two containing "Dehydrite" the latter two phosphorus pentoxide, were used. Since the gas mixture rapidly passed through the reaction tube, a long hot space was desirable, and the cold tube accordingly was allowed to extend only 6 or 7 cm into the heated zone, the resulting area of cooling surface being quite sufficient to collect the product.

The temperature of the reaction tube was raised gradually and at 600° a black deposit appeared on the tip of the cold tube. As the temperature approached 650° this deposit assumed a distinctly crystalline appearance, the crystals consisting of large thin plates as well as short needles, both *black* in color. When two or three grams of trichloride had collected on the cold tube the temperature was lowered to 300°, the stream of cold water shut off and the hydrogen current reduced to two bubbles per second. The flask containing the tetrachloride was warmed so as to allow these vapors to pass through in large quantities, in order that any dichloride present might thus be converted into the trichloride. When all the tetrachloride had vaporized, the slow hydrogen current was continued in order to remove any tetrachloride adhering to the trichloride or to the walls of the apparatus. The reaction chamber was then allowed to cool to room temperature and the hydrogen was displaced by dry, oxygen-free carbon dioxide. The traps containing the unchanged tetrachloride were then sealed off and by suitably rotating the reaction tube the black product was shaken down into a side tube, wherein it could be divided into two samples (each weighing about a gram) and sealed off.

The violet color hitherto ascribed to titanium trichloride is probably due to traces of moisture; when a sealed tube containing the black crystals is opened the color instantly changes to violet, although moist air has no apparent further effect for some time. The needles gave indications of being, in general, somewhat more reactive than the plates.

The action of heat on the trichloride was studied in a vacuum of approximately 0.001 mm. The temperature was raised slowly, and at 425–440° the crystals were observed to volatilize very gradually, thin transparent violet plates 3 or 4 mm. in diameter depositing just beyond the heated portion of the tube. The violet color in transmitted light is here due doubtless to the excessive thinness of the plates. At a slightly higher temperature, approximately 450°, the trichloride was observed to decompose, yielding the di- and tetrachlorides, the latter collecting as a white solid in the far end of the tube, which was chilled to −78°. While at 450° the decomposition was very slow, it proceeded at 475° at such a rate that a 1-g. sample required twelve hours for complete decomposition.

Attempts to prepare a dichloride of high purity failed, despite all precautions to exclude air and moisture. The purest sample obtained gave the following analysis: Ti, 41.5%; Cl, 56.4%; as compared with the calculated values. 40.4 and 59.6%, respectively. When the samples were treated with water, a small fraction, which proved to be elementary titanium, invariably remained unaffected. In order to determine whether this titanium was derived from decomposed dichloride, a specimen of the latter was introduced into one end of an evacuated tube and heated to 475°, the other end being chilled strongly. The appearance within a few hours of a white solid in the chilled end of the tube indicated that the reaction $2TiCl_2 = TiCl_4 + Ti$ had commenced. The volatility of the dichloride was next tested by heating in a vacuum over the range 300–600°, but at no time was any evidence of sublimation observed. The same experiment was repeated in an atmosphere of hydrogen, but the appearance of tetrachloride constituted the only noticeable change. The possibility that the dichloride is appreciably volatile *in vacuo* or in an atmosphere of hydrogen may therefore be excluded, and the hypothesis advanced by Meyer as to the mechanism of the reduction of the tetrachloride cannot be substantiated, The large amount of dichloride obtained was probably due to the decomposition of the trichloride at the high temperature employed.

Since the dichloride is slowly decomposed at 475°, it is hardly possible to prepare it in a state of purity by the method above described. Calculated on the basis of chlorine discrepancy, the decomposition of the dichloride we obtained amounts to approximately 5% of the original sampie. From the results of Ruff and Neumann the figures 8.4 and 9.2% are obtained, while the titanium content of Stähler and Bachran's dichloride ranged from 7.0 to 9.4%.

Reactions of Titanium Trichloride and Titanium Dichloride with Ammonia.—Georges and Stähler[8] reported that when titanium trichloride is shaken with liquid ammonia a yellow emulsion is formed, and part of the substance appears to dissolve, and Friedel and Guérin[7] studied the reaction between the dichloride and ammonia at red heat. In view of the fact that these substances are extremely reactive toward water, it is reasonable to suppose that they should react with ammonia at low temperatures.

In some preliminary experiments ammonia was conducted over the two chlorides at room temperature; both swelled up considerably and heat was evolved. The product formed was white in the case of the trichloride, but the dichloride yielded a pearl-gray substance. The experiments were repeated at −78° and the same results were noted. Two alternative modes of reaction are possible. The two chlorides may form molecular addition compounds, as is generally the case with halides of the metallic elements; or, as frequently happens with halides of non-metallic elements, mixtures of ammonium chloride and an amide or imide of the non-metal (depending on the temperature) may be formed. Stähler and Wirthwein[8] have reported the formation of titanic tetramide by the interaction of the tetrachloride with liquid ammonia. With titanium in its lower valences it is of interest to determine whether, accompanying the increase in basigenic character of the element, the formation of true ammines becomes possible. The following experimental work, undertaken from this point of view, proves such to be the case.

Reaction of Titanium Trichloride with Ammonia.—The apparatus used was a modification of that which Thomas and Pugh[9] recently have employed in similar work on germanium tetrachloride. This apparatus allowed ammonia to act on the chlorides at any temperature between −78° and room temperature, and also permitted the product formed to be thoroughly stirred and washed several times in liquid ammonia, so that any ammonium chloride might be removed. In order to be sufficiently dried, the entire apparatus was alternately thoroughly evacuated and filled with dry carbon dioxide. This gas was taken from a ten-liter reservoir, which was equipped with a manometer and filled from a cylinder after passage of the gas through a purifying train to remove oxygen and moisture. The trichloride was introduced from one of its sealed containers by opening one end and rapidly attaching it to a piece of heavy-walled rubber tubing, the other end of which was connected to the open tube (a), shown in the accompanying figure The system was evacuated and refilled with carbon dioxide. The trichloride was shaken down into the 26-mm. reaction tube (b) and the tube (a) sealed off as indicated. The major portion of the crystals was caught in the shallow, heavily gold-plated copper dish *(c)*. This dish, about two mm. less in diameter than the reaction tube, was held in place

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(7) Friedel and Guérin, *Ann. chim. phys.*, [5] 8, 24 (1876).

(8) Stahler and Wirthwein, *Ber.*, 38, 2619 (1905).

(9) Thomas and Pugh, J. *Chem. Soc.*, 61 (1931).

by indentations in the glass above and below, but was free to move vertically about two mm. The reaction tube was surrounded by a cylindrical vacuum jacket closed at the lower end with a rubber stopper. Connection between the receiver (d) and the reaction tube was at first made through a wide-bore stopcock, but this proved unsatisfactory, as when liquid ammonia filled the tube fissures formed in the lubricant, causing leakage of air. The connection was subsequently made with a thick-walled rubber tube, closed with the screw-clamp (g). The ammonia was conveyed from a cylinder into an evacuated bulb (e), where it was condensed and dried with sodium. Approximately one quarter of the liquid was then evaporated, the vapor, sweeping out any air and hydrogen, escaping through the mercury trap (f), which was arranged to serve as a manometer as well.

The cylindrical vacuum jacket surrounding the reaction tube was cooled to −78°, the system evacuated with the screw-clamp (g) closed, and ammonia slowly admitted from (e). The trichloride swelled up to form a spongy mass, six or seven times its original volume, with but slight change in color. Ammonia was allowed to condense until the liquid entirely surrounded the spongy mass, which gradually collapsed to form a grayish powder. The supernatant liquid had a yellow color, as Georges and Stähler reported, but it was less pronounced after the second treatment and finally disappeared altogether. As the liquid was allowed to warm violent bumping commenced, and the vibrations of the dish caused the powder to be thrown about in it. This provided a means of thorough stirring; as the temperature was lowered the bumping ceased, and as the powder settled all but a small portion was caught in the dish. After this stirring process had been repeated a few times and the pressure of the ammonia had become atmospheric, the screw-clamp (g) was opened and the liquid passed down into (d), where it was allowed to evaporate. The clamp was closed, the reaction chamber again filled with liquid ammonia, and the above operations were repeated four or five times. The total time of exposure to ammonia was in no case less than twelve hours. If a mixture of imide and ammonium chloride had been formed, there was thus ample time and opportunity for the latter to be leached out by the liquid. After the last treatment the reaction tube was allowed to warm up to room temperature, the ammonia escaping through the mercury trap. In the first few experiments the ammonia was replaced by carbon dioxide; both gases were sufficiently dry to prevent any observable reaction between them. When the apparatus was completely filled with the latter gas, it was turned to a horizontal position and the product divided into two samples, which, one at a time, were shaken down into (a) and sealed off.

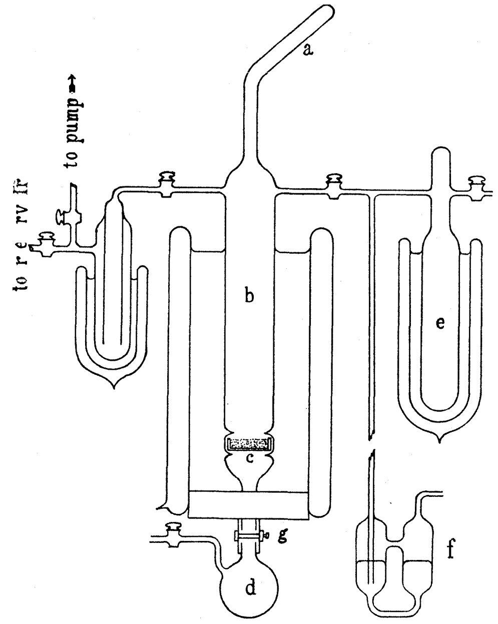

Fig. 1.

The product thus obtained is white, though grayish when moistened with liquid ammonia, and reacts violently with water—more so, in fact, than is the case with the trichloride itself. When kept in a sealed tube in an atmosphere of carbon dioxide it darkens perceptibly within a day or two; hence it was preserved in an atmosphere of ammonia, even though this introduced complications in the subsequent analysis.

Analysis.—The sample was dissolved in dilute nitric acid and then boiled with an excess of alkali, the ammonia being collected in a known amount of acid. The apparatus consisted of a three-necked Woulfe bottle, through one neck of which the sample was introduced, while through a second neck alkali was admitted from a separatory funnel. The liberated ammonia was conveyed through a splash bulb and a condenser into an Erlenmeyer flask containing the acid, the excess of which was then determined by titration, using methyl red as indicator. This method was shown to yield sufficiently accurate results by separate experiments with known weights of pure ammonium chloride.

The sealed glass tube containing the sample to be analyzed, together with some free ammonia, was weighed and opened, correction being made for the buoyancy of the gas.[10] The open end was rapidly inserted into one neck of the thoroughly dried Woulfe bottle, while a counter current of dry air through the apparatus swept out the same neck. The free ammonia, lighter than air, was thus rapidly swept out in a few minutes by the air current. The neck was then closed by a rubber stopper and 2 *N* nitric acid slowly admitted from the funnel until a clear solution was obtained. Sodium hydroxide solution was added in considerable excess and water to make the volume 200 cc. The liquid was carefully boiled until its volume had been reduced to 50 cc., this operation requiring about two hours. The excess acid was then titrated with carbonate-free sodium hydroxide.

The liquid remaining in the Woulfe bottle was diluted and acidified with nitric acid. A precipitate containing titanium hydroxide and silicic acid (derived from the glass) appeared. This was filtered off, silver nitrate was added, and the chlorine determined in the usual manner. Titanium was not determined in the above-mentioned precipitate, but separate samples were dissolved in dilute nitric acid, the titanium precipitated with ammonia, washed, dried, ignited and weighed as TiO_2. The chlorine was also determined in these samples (I and II, below). The results agree reasonably well with the values calculated for titanium trichloride hexammine.

	I	II	III	IV	Calcd. for $TiCl_3·6NH_3$
Ti	18.82	18.59	...	...	18.69
Cl	40.94	41.17	41.11	41.66	41.50
NH_3	...	...	39.74	39.58	39.81

Properties.—Titanium trichloride hexammine is a white powder which reacts violently with water, yielding the familiar solution of trivalent titanium. It dissolves in dilute nitric acid to form a clear solution. When exposed to air it smells strongly of ammonia and darkens rapidly. In a sealed tube filled with dry carbon dioxide it darkens less rapidly, but nevertheless appreciably.[11] It decomposes even when preserved in contact with dry ammonia at atmospheric pressure. Thus after a week a 0.8332-g. sample so preserved contained only 36.6% of ammonia. When gently heated in a vacuum it readily gives up four moles of ammonia and turns black, but the remaining two moles appear to be held tenaciously. The

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(10) As the tubes were never more than 12 cc. in volume, they contained less than 0.01 g. of free ammonia.

(11) After five days a 0.5037-g. sample kept in a 12-cc. tube showed but 32.4% NH_3.

resulting black substance is so reactive that it catches fire on exposure to moist air.

The thermal decomposition of the hexammine was studied quantitatively. The ammonia set free by heating the substance in a Wood's metal bath at 300° was condensed in a bulb immersed in liquid air. When the decomposition appeared to be complete, as indicated by the color of the residue and by the fact that no further ammonia condensed, the bulb was sealed off and the weights of the black residue and ammonia were determined. The percentages of ammonia released from the original samples correspond to 4.08 and 4.15 moles, respectively.

	Wt. residue	Wt. NH_3	% NH_3 evolved from orig. sample
I	0.4743	0.1760	27.07
II	1.2390	.4722	27.53

The black residue was then analyzed for titanium and chlorine in the usual manner, but the content of ammonia, though its presence was shown qualitatively, was determined by difference. This difference was calculated on the assumption that the original material before heating contained 39.81% of ammonia From this amount the weight of ammonia condensed by the liquid air was deducted, after the necessary corrections for the presence of free ammonia in the sample tube had been made.

	I	II	Calcd. for $TiCl_3 \cdot 2NH_3$
Ti	26.1	26.4	25.5
Cl	55.7	56.0	56.4
NH_3	17.5	16.9	18.1

Although the evidence offered by the preceding analyses is not considered sufficient to afford conclusive proof of the existence of a diammine of titanium trichloride, it indicates that on gentle heating the hexammine gives off four moles of ammonia, and the resulting substance is probably a diammine and not a chloronitride, such as Ruff and Eisner reported in the case of the decomposition of the tetrachloride hexammine.[12] As the temperature is raised, no more ammonia is set free, and finally a second decomposition occurs, involving the disintegration of the trichloride. Ammonium chloride was identified as one of the products.

Reaction of Titanium Dichloride with Ammonia.—The apparatus and procedure employed was the same as that used with the trichloride. The dichloride was in contact with liquid ammonia for a period of twelve hours, during which time the material was thoroughly stirred and washed five or six times. Because the dichloride is a fine dry powder, as compared with the comparatively large crystals of the trichloride, a larger amount was lost during the stirring operations, and therefore the samples were rather small.

(12) Ruff and Eisner, Bn., 41,2280 (1908).

In other respects the dichloride behaved as did the trichloride; the product, however, was pearl gray rather than white.

Analysis.—The method of analysis for ammonia and chlorine was that used with the corresponding compound of the trichloride. A Pyrex Woulfe bottle, which was found to be resistant to the action of a boiling alkali solution, was employed, and the amount of silica dissolved was sufficiently small to allow the determination of titanium in the same sample Before the final weighing of titanium dioxide, any silica that might possibly be present was volatilized by heating with hydrofluoric and sulfuric acids.

Due to the difficulty of obtaining specimens of titanium dichloride free from both the trichloride and elementary titanium, the samples of reaction product were never wholly pure. Inasmuch as elementary titanium does not react with ammonia under the conditions used, it was thought less objectionable to work with samples containing 5% of free titanium, rather than with samples containing small amounts of trichloride. When samples of the reaction product were treated with water a small fraction remained unaffected, as with the dichloride itself, but as the solution above was always turbid from hydrolysis, it was not feasible to separate the free titanium by filtration. The content of elementary titanium in the samples was determined by independent analysis of the original dichloride, and also by noting the amount of titanium in the reaction product in excess of the atomic ratio 1:2. Both methods gave approximately the same results, the composition of the product corresponding reasonably well with the formula $TiCl_2 \cdot 4NH_3$.

	I	II	III	Calcd. for $TiCl_2 \cdot 4NH_3$
Ti	25.26	25.10	25.73	25.63
Cl	37.26	37.14	37.34	37.92
NH_3	35.83	36.61	36.13	36.45

Properties.—Titanium dichloride tetrammine as thus obtained is a pearl-gray powder which smells strongly of ammonia when exposed to air. It dissolves in water with the evolution of hydrogen, yielding a dark brown, turbid solution, but the reaction is slower than that of the dichloride itself. Dilute nitric acid dissolves it with a hissing sound, forming a yellow solution which is not quite clear, and as in the case of the water solution minute particles of elementary titanium remain undissolved. When heated at 300° in a vacuum it gives off ammonia, ammonium chloride appearing simultaneously. This was driven to the cooler parts of the tube, and when the decomposition appeared to be complete the black residue was sealed off and analyzed. It was found to contain approximately 60% of titanium, and is presumably a nitride; a sample free from chlorine was never obtained, five or six per cent. of the latter invariably remaining despite continued heating. The presence of nitrogen was shown qualitatively, but specimens sufficiently pure to justify a quantitative analysis could not be obtained.

The authors are indebted to Dr. E. Lee Gamble for kind assistance in some of the analytical work.

Summary

Anhydrous titanium trichloride, prepared by the reduction of the tetrachloride with hydrogen at 650°, exists in two crystal forms, plates and needles, both *black* in color in reflected light. Exceedingly thin plates show a violet color in transmitted light. The data of Ruff and Neumann relating to the behavior of the trichloride when heated in a vacuum are confirmed.

Anhydrous titanium dichloride, prepared by the thermal decomposition of the trichloride, is slowly decomposed when heated in a vacuum to 475°. Therefore specimens of the dichloride so prepared are inevitably contaminated with free titanium. No evidence of volatility is obtained when the dichloride is heated over the range 300–600°, either in a vacuum or in an atmosphere of hydrogen. The hypothesis concerning the mechanism of reduction of the tetrachloride by hydrogen, advanced by Meyer, Bauer and Schmidt, therefore cannot be substantiated.

The trichloride combines with ammonia at low temperatures to form a white hexammine. Liquid ammonia does not dissolve out any ammonium chloride, despite prolonged stirring and washing. The possibility that the compound is not a true ammine, but rather a mixture of an imide and ammonium chloride, is therefore excluded. On heating to 300° the hexammine readily gives off four moles of ammonia, a reactive, black substance, probably a diammine, remaining behind.

The dichloride likewise reacts with ammonia at low temperatures, yielding a pearl-gray tetrammine, the properties of which are in general similar to those of the hexammine of the trichloride.

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The Dissociation Pressures of Magnesium Ammonium Phosphate Hexahydrate and Some Related Substances. VII

BY SAMUEL J. KIEHL AND HENRY B. HARDT

In 1847 Heintz[1] published a method for the determination of magnesium or phosphorus based upon the precipitation of these elements as magnesium ammonium phosphate hexahydrate and the ignition of it to magnesium pyrophosphate. This method, as improved by Gibbs[2] in 1873, has come into very general use. It was and is, however, subject to a large number of possible errors, and there have appeared, therefore, in the last sixty years ninety or more research reports upon its various phases. The facts brought out by these studies fall mainly into two groups: those dealing with the conditions necessary to the quantitative precipitation of the magnesium or phosphorus in the form of pure $MgNH_4PO_4 \cdot 6H_2O$; and those dealing with the ignition of this precipitate to $Mg_2P_2O_7$. The subject has been attacked from almost every conceivable angle.

Nevertheless there remains still a need for some information which may be deemed important for the ignition of the hexahydrate. It seems noteworthy that, although the salt precipitated is a hydrate which loses its water of hydration during the ignition process, there should be a lack of information upon its dissociation pressure. Furthermore, it is not only a hydrated ammonium salt which loses both its water of hydration and its ammonia, but also an orthophosphate which is converted to a pyrophosphate by the loss of water of constitution. Consequently we believe that a knowledge of the pressure developed in the reactions involved during heating will help to ensure an intelligent manipulation of an operation which is so vital a part of a quantitative procedure.

It seems probable, therefore, that a study of the dissociation of magnesium ammonium phosphate from the viewpoint of the phase rule may yield valuable information. According to the phase rule, a salt hydrate that dissociates into a lower hydrate or an anhydrous salt and a gaseous phase is a two-component system, and with three phases present it is univariant. A large number of such systems have been studied and reported in the literature by a number of very able investigators. Among those who have done much in this field to improve the method for measuring dissociation pressures of such systems are: Johnston,[3] whose excellent apparatus and method present a real improvement, Baxter and Lansing, Frowein, Menzies and Wilson.[4] The last two mentioned give good criticisms of the

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(1) Heintz, *Pogg.* Ann., 73, 137 (1847)

(2) Gibbs, *Am.* J. *Sci.*, [3] 5, 115 (1873).

(3) Johnston, Z. *physik. Chem.*, *62*, 330 (1908).

(4) Baxter and Lansing, THIS JOURNAL, **42**, 419 (1920); Frowein, *Z. physik. Chem.*, *1*, 5 (1887); Menzies, THIS JOURNAL, 42, 1952 (1920); Wilson, *ibid.*, 43, 704 (1921).

many preceding researches and list the errors often made in manipulation and measurement.

The studies referred to above deal with univariant systems. Magnesium ammonium phosphate hexahydrate also forms such a system when it dissociates into a lower hydrate and water. However, in its case there is a further dissociation which yields a magnesium acid phosphate and ammonia and forms a third solid phase and a third component. This system, consisting of three components present in four phases, is also univariant and has, therefore, a definite dissociation pressure at any fixed temperature. Therefore both the two-component and three-component systems are represented in this investigation. Systems 1, 4 and 5 listed below consist of two components, while systems 2 and 3 contain three components. The following systems were studied

System 1. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O
System 2. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3
System 3. $MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O
System 4. $MgHPO_4 \cdot 7H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O
System 5. $MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

Preparation and Analysis of Materials

$MgNH_4PO_4 \cdot 6H_2O$.—Equivalents of $Na_2HPO_4 \cdot 12H_2O$, carefully purified, and magnesia mixture (usually about one liter of each, of one-tenth molar concentration), were mixed and the precipitate dissolved in hydrochloric acid. Very dilute ammonium hydroxide was then added slowly with constant stirring until the salt was almost all precipitated. Then more concentrated ammonium hydroxide was added until its concentration was approximately one molar. After standing for four hours or more, it was washed with water until a sample of it dissolved in one-tenth molar nitric acid gave no test for chloride with siliver nitrate. After it was filtered on a hardened filter paper in a Buchner funnel and washed with four 50-cc. portions of absolute ethyl alcohol, then with four 50-cc. portions of anhydrous ether, it was transferred to a bottle where suction was applied by means of an oil pump for an hour. The salt adhering to the filter paper was rejected to reduce the danger of organic impurities. By this method a number of lots were prepared, all of which were shown by the microscope to be distinctly and uniformly crystalline, gave the theoretical loss in weight on ignition closer than one part per thousand, gave the theoretical percentage of ammonia within one part per thousand and gave snow-white residues on ignition.

$MgNH_4PO_4 \cdot H_2O$.—This salt was prepared by the same method as the hexahydrate, except that it was precipitated from boiling solution, kept in an oven in the mother liquid at 100–102° for twenty-four hours, washed with boiling water, and dried in an oven at 106° for eight hours. It was very uniformly crystalline, consisting of square, flat crystals, gave the theoretical loss in weight upon ignition, the theoretical ammonia content, and snow-white residues upon ignition.

$MgHPO_4 \cdot 7H_2O$.—Equivalents of $MgSO_4 \cdot 7H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ in solutions were mixed; the precipitate was dissolved by adding a small amount of sulfuric acid, and reprecipitated by adding slowly a dilute sodium hydroxide solution. The salt was washed with water, alcohol and ether, dried on a glass plate until free from ether, and bottled. It consisted of large needle-shaped crystals which gave the theoretical loss of weight upon ignition. This hydrate is very unstable. Further comment will be made later.

$MgHPO_4\,3H_2O$.—When the $MgHPO_4{\cdot}7H_2O$ still in its mother liquid was warmed to 35°, the long needle-like crystals changed to the rhombic form. Upon ignition these gave the theoretical loss in weight for the reaction $2MgHPO_4\,3H_2O \rightleftarrows Mg_2P_2O_7 + 7H_2O$ and a snow-white residue.

Apparatus

The apparatus used for the measurement of pressures is an adaptation of that of Kiehl and Wallace,[5] which was a modification of that of Johnston.[3] Some of the systems, in fact, may well be measured with practically the same arrangement. The first salt studied, $MgNH_4PO_4\,6H_2O$, however. has such an exceptionally high dissociation pressure that with this form of apparatus it was impossible to prevent the condensation of the water. The water vapor pressure produced was so near that of water itself that even a slight difference of temperature between the furnace and the steam-jacket caused condensation in the cooler portion of the system within the steam-jacket.

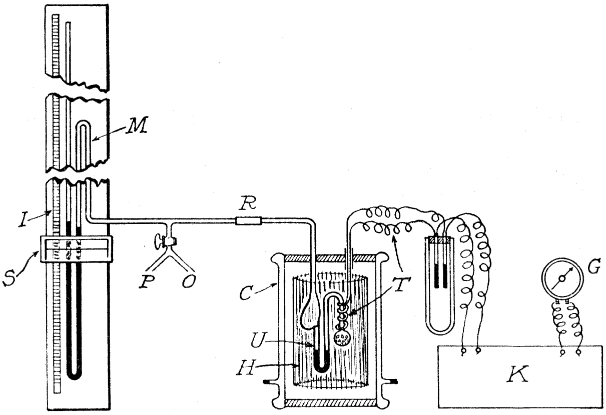

Fig. 1A.—Apparatus for the measurement of dissociation pressures.

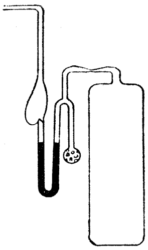

Fig. 1B.—Modified manometer used in determining the ratio of water to ammonia in the vapor phase.

A modification was made, therefore, whereby this condensation was prevented, the arrangement was simplified, and manipulation made much easier. The essentials of the apparatus are shown in Fig. 1A. The furnace and steam-jacket formerly used were combined into a unit consisting almost entirely of Pyrex glass and a resistance wire. A double-walled cylinder, C, of heavy Pyrex glass, with a vacuum between the walls, 27 centimeters long and 6.5 centimeters inside diameter was used as a chamber for the heater. The ends were closed with corks covered with heavy asbestos paper. The heating unit. H, consisted of a smaller Pyrex cylinder upon which was wound 27 feet of 28-gage nichrome wire. When this heater was connected with the 110-volt circuit, any temperature from room temperature up to 425° could be secured by use of appropriate resistance.

The manometer, M, described heretofore,[5] was connected to an oil pump, by which a vacuum of 0.2 mm. pressure could be secured. When pressures less than one atmosphere were to be measured, an air valve at O was used to admit air to counterbalance the pressures developed by the system; and for pressures greater than an atmosphere and for

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(5) Kiehl and Wallace, THIS JOURNAL, 49,375 (1927).

Wood's metal as a confining liquid, O was connected to a high-pressure hydrogen cylinder by means of heavy-walled rubber tubing which was wrapped tightly with tire-tape. The connection, R, was also wrapped pressure tubing, which permitted tilting the furnace after evacuation. Before it was wrapped the rubber tubing was thoroughly massaged several times, inside and out, with warm castor oil, to make it less permeable to gases. This oiled and wrapped pressure tubing retained pressures of five and one-half atmospheres satisfactorily.

As a confining liquid for the gases formed by the dissociation, mercury is usually the best because it is the least likely to absorb or react with the gases present. In this investigation it was found very satisfactory for low temperatures. Since the nature of the systems measured and the method and apparatus used required the confining liquid to be kept at the same temperature as the system itself, and since mercury boils at 357°, a large correction due to the vapor pressure of mercury thereupon would be required as the temperature approached this point. Besides, as the temperature rose, the mercury would distil from the capillary and condense in the cooler portion of the tube.

In looking for a confining liquid that did not have this limitation at higher temperatures, Wood's metal proved to be excellently suited. It has practically no vapor pressure at the temperatures where its use was required. When a sample of the purest material obtainable was placed alone in the dissociation pressure apparatus no appreciable pressure developed at even the highest temperature used for measuring dissociation pressures. When, however, the temperature was increased to 300°, a pressure of 5 millimeters was developed. Two limitations should be mentioned in connection with its use. At higher temperatures especially, a troublesome scum will form upon the surface of the metal if air is allowed to come in contact with it. Hydrogen was therefore used to counterbalance the pressure developed in the system. The metal should not be allowed to solidify in the capillary as the strain produced by the contraction of the cooling glass and by the solidification of the metal may break the small manometer. After the completion of the experiment the metal in the liquid state may be transferred to the properly constructed reservoir.

A chromium-plated strip of brass 1.9 cm. wide by 7.6 cm. long with a millimeter scale engraved upon it was attached to the legs of the differential manometer within the heater to aid in leveling the confining liquid.

For reading temperatures up to 350° a copper–constantan thermocouple was employed. Above that temperature a platinum–platinum-rhodium thermocouple was used. The thermocouples were standardized against the melting points of samples of tin, lead, zinc and aluminum from the United States Bureau of Standards, the boiling points of water, alcohol and ether and the freezing point of water. A water and ice cold junction was used. The instruments and method of measurement were described heretofore.[5]

For beating the salts in *vacuo*, a thick-walled Pyrex tube 40 cm. in length and 5 cm. in diameter, with a ground-glass cap which was fitted with a stopcock, was used. The lower third was placed in an electric furnace and the upper part protected from the heat of the furnace by two tightly fitting asbestos stoppers, so that when evacuated the lower part could be heated to above 450° while the upper end remained at room temperature. A platinum crucible containing the salt was lowered into the tube by means of a glass rod bent at the bottom into the form of a ring.

For the ignition, when they were required, porcelain Gooch crucibles were used in an electrically heated muffle-furnace.

Method

Dissociation Pressures.—The well-known static method for measuring dissociation pressures of salt hydrates was employed. The bulb, filled with a sufficiently large sample of the salt (0.1 to 0.25 *g.)* was sealed to the small manometer. When mercury was used as a confining liquid it was poured into the reservoir, and the manometer connected at R. The system was then evacuated and left overnight. The next morning the system was again evacuated and the mercury tilted into the capillary. Then the heat was turned on and the desired temperature maintained until the pressure became constant. All reactions attained equilibrium in a reasonable time; the longest time required was about sixty hours, in the case of System 1 at low temperatures, which was unusual. When Wood's metal was used the procedure was exactly the same except that the system **was** heated to 75–100° before the liquid was introduced. When constant pressure had been reached and maintained without change for an hour or more it was recorded; the temperature was then increased and the new equilibrium pressure found. When the highest pressure to be measured had been determined, the process was reversed; that is, the temperature was reduced stepwise, and the pressure found for each temperature. The temperature–pressure curve was considered a true equilibrium curve only when the curve for increasing temperatures coincided with that for decreasing temperatures. The same equilibrium pressure therefore was obtained when approached from either lower or higher temperatures.

The entire experiment was then repeated with a mixture of the substance being studied and the solid phase or phases believed to have formed during dissociation. When no irregular behavior from the beginning throughout the temperature range occurred and when the curve thus obtained was the same as that for the original salt alone, evidence for the identity of the solid phase was established and the equilibrium curve confirmed.

Evidence for Phases Present

Since no distinctive tests are known by which the hydrates of $MgNH_4PO_4$ and of $MgHPO_4$ may be identified when in the presence of each other, it is necessary to establish the presence of all phases by reasoning from the results obtained. The evidence showing which substances are formed by the dissociation in each system is given below.

System 1. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O

1. The monohydrate is formed from the hexahydrate and it may be isolated in fairly pure form if the gas evolved at 50° or less is removed as it is liberated.

2. Red litmus in the reaction chamber does not change to blue below 50°, nor does it change when moistened and exposed to the gas which has been removed from the reaction chamber. Ammonia is not given off below 50°.

3. The hexahydrate forms monohydrate because the two when mixed give the same curve as the hexahydrate alone.

System *2.* $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3

1. The monohydrate is formed from the hexahydrate and it may be isolated in fairly pure form if the gas evolved at 50° or less is removed as fast as it is formed.

2. $MgNH_4PO_4 \cdot H_2O$, when heated in a closed system under the high vapor pressure of water furnished by the hexahydrate, first loses ammonia, forming $MgHPO_4 \cdot H_2O$ (see System 3), but under the conditions prevailing here, the monohydrate is converted to the trihydrate, because the trihydrate is the salt in whose range of existence the pressure–temperature curve for System 2 lies.

3. The water and ammonia, on cooling, form a solution which quickly turns red litmus blue, and smells strongly of ammonia.

4. A mixture of the first and second, or first, second and third, solid phases gives the same curve as the first alone.

System 3. $MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O

1. Either zinc acetate reagent or silver nitrate gives tests for pyrophosphate[6] whenever both ammonia and water are found in the gaseous phase.

2. When $MgNH_4PO_4 \cdot H_2O$ is heated in an open vessel so as to drive off a part of the volatile matter, it always retains a larger percentage of its NH_3 than of its H_2O as shown below:

Temp. to which heated, °C.	340	335	350	380
NH_3 retained, %	24.5	29.5	17.0	6.0
H_2O retained, %	17.3	24.0	12.0	2.0

This shows that the water of hydration may be expelled while some of the ammonia still remains in the form of anhydrous ammonium salt.

3. When $MgNH_4PO_4 \cdot H_2O$ is heated in the temperature–pressure apparatus, and the gaseous phase at equilibrium is analyzed, the ratio of water to ammonia is found to be about 3:1. Data are tabulated under "Experimental Results." These analyses show that some of the substance which has lost water has not lost ammonia. Each molecule of $MgNH_4PO_4 \cdot H_2O$ contains but one molecule of water of hydration for every molecule of ammonia.

4. The system at equilibrium always gives positive tests for pyrophosphate whenever ammonia is present.

5. Mixtures of the first and second, or first, second and third, phases give the same pressure–temperature curve as the first alone.

System 4. $MgHPO_4 \cdot 7H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O

1. If the vapors formed are pumped off, it is found that there is a great decrease in pressure at equilibrium when the composition of the resulting solid is approximately $MgHPO_4 \cdot 3H_2O$.

2. Crystals appear which have the same form as those of pure $MgHPO_4 \cdot 3H_2O$.

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(6) Kiehl and Coats, THIS JOURNAL, 49, 2180 (1927)

3. Either the heptahydrate or a mixture of the two hydrates gives the same curve.

System 5. $MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

1. Zinc acetate reagent does not give a test for pyrophosphate even when a great pressure has been developed. (This reagent, consisting of a thirty-two hundredths molar zinc acetate solution in the presence of one-eighth its volume of glacial acetic acid, has been shown by Kiehl and Coats[7] to be sufficiently sensitive to detect 0.0006 molar pyrophosphate in the presence of 0.1 molar orthophosphate.

2. If the vapors formed are pumped off, it is found that there is a great decrease in equilibrium pressure when the composition of the resulting solid is approximately $MgHPO_4 \cdot H_2O$.

Determining the Ratio of Water to Ammonia.—To determine the ratio of water to ammonia in System 3 where both of these substances are liberated as gases, the following method was used. A receptacle resembling a large test-tube was sealed to the bulb containing the salt as shown in Fig. 1B. There was a constriction in the tube which connected the bulb to the remainder of the apparatus to facilitate sealing off the bulb when equilibrium was established. In addition to the regular stopper in the top of the furnace, an extra asbestos stopper with a small hole just over the constriction in the tube was used.

The apparatus was arranged in the usual way except that the salt bulb contained about a gram of salt instead of the usual 0.2 to 0.3 g. charge. When equilibrium was established the temperature was noted, the extra stopper of the furnace removed, and the large bulb quickly sealed off with a small, hot flame. This could be done with practically no change in temperature, and with the leveling liquid showing no change in position. The bulb was then inserted into a measured volume of 0.02 N sulfuric acid and the tip broken off. The excess acid was back-titrated with 0.02 *N* sodium hydroxide and the standard volume of the ammonia as a gas was calculated. The standard volume of all the gas present was also calculated and the water determined by difference. The method worked very satisfactorily up to a total pressure of one atmosphere.

Experimental Results

The temperature–pressure data for four runs on each system studied are given in the following tables. All pressures are recorded in millimeters of mercury at 0°.

In order to select from the temperature–pressure data recorded above those values which would as nearly as possible represent the value most probable for each temperature in each system, the following method was used. From the data for each of the four runs a curve was drawn; from these four curves, one pressure corresponding to the average of the four

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(7) Ref. 6, p. 419.

TABLE I

EXPERIMENTAL DATA FOR SYSTEMS 1 AND 2

$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O (below 60°)
$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3 (above 60°)

Run no. 1		2		3		4	
T, °C.	*P*, *mm.*	*T*, °C.	*P*, *mm.*	*T*, °C.	*P*, *mm.*	*T*, °C.	*P*, *mm.*
41.1	34.2	39.0	32.1	40.0	35.0	42.3	34.9
50.0	71.1	51.9	83.0	51.6	77.0	55.5	79.9
53.5	78.2	59.0	100.0	55.4	89.3	57.0	88.9
62.0	122.5	59.9	113.0	59.0	106.3	61.5	117.5
65.0	144.8	63.6	133.4	61.5	121.4	66.0	139.5
73.0	205.1	65.0	154.8	62.8	126.7	77.1	275.4
85.0	377.9	71.2	196.2	68.1	162.1	86.0	390.6
87.0	407.9	75.0	242.2	69.2	169.9	102.5	710.1
89.5	450.7	88.3	450.8	74.0	220.0	118.9	1208.1
94.0	513.0	100.1	670.1	81.9	292.2	119.6	1240.8
108.0	846.8	106.2	823.0	88.5	373.4	132.0	1809.8
112.5	957.0	115.2	1020.0	89.6	423.2	133.6	1941.5
125.6	1423.0	125.6	1448.8	102.2	704.6	135.1	2008.0
128.5	1620.0	137.0	2113.3	103.4	713.9	139.6	2264.1
131.0	1734.0	140.5	2271.7	111.9	948.8	146.0	2536.0
132.5	1838.0	146.2	2655.0	112.6	952.6	152.8	3273.3
134.8	1926.0	152.4	3263.3	118.0	1151.1		
136.5	1950.0	156.2	3696.7	120.0	1238.7		
150.0	2846.0			120.5	1278.9		
152.8	3423.0			134.4	1969.9		
				140.5	2352.0		
				142.6	2385.0		
				159.1	3834.0		

TABLE II

EXPERIMENTAL DATA FOR SYSTEM 3

$MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O

Run no. 1		2		3		4	
T, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*. °C.	*P*, *mm.*	*T*, °C.	*P*, *mm.*
121.9	9.0	131.7	11.1	127.8	9.8	125.0	9.5
131.0	11.1	145.5	18.9	131.9	12.2	132.7	14.7
165.0	52.8	152.8	24.9	137.4	13.9	138.0	17.5
209.8	217.4	159.9	35.0	149.1	22.5	163.8	45.3
227.5	353.3	183.6	87.4	164.8	43.9	175.1	64.8
246.5	684.9	198.7	141.0	175.7	62.8	186.6	90.8
253.3	908.5	227.0	311.8	188.4	97.2	195.1	136.2
261.6	1280.0	250.2	735.4	199.2	143.8	203.0	174.5
270.8	1888.0	265.0	1389.0	210.7	207.7	215.5	235.8
279.9	2873.4	270.0	1839.6	231.0	369.1	230.9	392.0
280.9	3187.4	274.9	2400.0	250.0	767.5	258.9	1145.0
281.9	3429.4	279.1	2929.0	254.8	1117.0	272.8	2209.0
				274.0	2514.2	279.5	3089.0
				281.6	3327.2		

values, one for each curve taken at ten degree intervals was obtained. From these average values recorded in Table IV, the final curve in Fig. 2 for the system was drawn.

TABLE III

EXPERIMENTAL DATA FOR SYSTEM 5

$MgHPO_4{\cdot}3H_2O$, $MgHPO_4{\cdot}H_2O$, H_2O

Run no. 1		2		3		4	
T, °C.	P, mm.	T, °C.	P, mm.	T, °C.	P, mm.	T, °C.	P. mm
33.0	10.5	51.0	26.2	44.0	17.5	27.0	10.0
41.0	13.0	54.0	31.5	49.9	25.8	32.0	12.2
49.0	21.1	62.0	43.5	51.0	27.1	42.0	14.7
59.5	32.2	76 1	72.2	55.0	32.5	51.0	25.1
70.0	53.5	88.0	116.6	61.4	42 0	61.5	36.0
87.7	106.6	102.6	168.2	69.0	61.0	78 0	71.5
94.6	133.5	114.3	243.6	76 6	80.0	87.0	109.8
106.0	195.0	131.8	384 6	81.0	85.2	105.0	189.1
110.8	227.7	135.0	410.7	88.0	116.6	114.0	251.0
119.0	282.4	145.0	502.6	110.0	218.4	131.9	389.6
130 0	372.2	150.8	604.0	111.4	240.9	135.0	413.6
143.1	514.2	155.5	684.0	133.0	404.4	157.0	696.1
151.2	602.2	158 5	1300.0	156.0	691.0	159.0	1470.0
154.5	697.6						
159.0	1500.0						

TABLE IV

AVERAGE PRESSURES FOR SYSTEMS STUDIED AT TEN DEGREE INTERVALS

Pressure is given in millimeters of mercury at 0°

Systems 1 and 2		System 3		System 5	
T, °C.	P, mm.	T, °C.	P, mm.	T, °C.	P, mm.
40.0	33.4	130	11.2	30	9.9
50.0	69.8	140	16.2	40	14.1
60.0	109.0	150	24.3	50	24 3
70.0	177.5	160	36.9	60	37.3
80.0	302.3	170	55.9	70	59.7
90.0	450.0	180	78.5	80	85.0
100.0	651.9	190	111.4	90	120.2
110.0	901.5	200	149.8	100	165.4
120.0	1242.0	210	202.5	110	221.4
130.0	1688.0	220	276.9	120	289.6
140.0	2266.0	230	376.1	130	371.2
150.0	2935.0	240	530.7	140	467.2
155.0	3521.0	250	765.9	150	591 9
159.1	3834.0	260	1191.0	155	669.0
		270	1874.0		
		280	3129.0		

Determining the Ratio of Water to Ammonia.—The ratio of water to ammonia in the vapor phase at equilibrium for System **3** was determined at those temperatures at which the dissociation pressures were approximately one atmosphere and one-half an atmosphere. The analysis of the mixtures at these pressures gave the following results.

Discussion of Errors

1. By means of the silver scale and the hair-lined glass which is mounted in a steel frame and slides on a steel rod the manometer may be read to 0.2

TABLE V

THE RATIO OF WATER TO AMMONIA IN THE VAPOR PHASE OF SYSTEM 3 AT EQUILIBRIUM

				At 0° and 760 mm.		Percentage by volume	
	Vol. of gas collected, cc.	Temp., °C.	Total pressure,	Vol. of gas collected, mm.	Vol. of NH_3 by titration, cc.	ammonia, cc.	water vapor
1	52	246	726	28.24	7.82	27.71	72.29
2	52	245	695.8	26.11	6.77	25.95	74.05
3	52	245.3	703.6	25.62	6.65	25.97	74.03
						Av. 26.54	73.46
4	52	229	347.1	12.91	3.45	26.71	73.29
5	52	229	340.9	12.26	3.31	26.59	73.41
6	50	230	340.0	12.17	3.27	26.85	73.15
						Av. 26.72	73.28

The calculated values in the above table were obtained by use of the gas laws uncorrected.

mm. or less. Since most of the pressures read were high, the percentage errors due to this were low. For the lowest readings recorded this is not more than two per cent., while for all readings above 20 mm. it is less than one per cent.

2. The error due to leveling the confining liquid was not more than 0.1 mm., for the two arms of the manometer, very close together, are immediately in front of a bright, metallic millimeter scale.

3. It is impossible to remove all the absorbed air from the system. This is always an error in measuring dissociation pressures by the static method; but, while it cannot be eliminated, it is greatly reduced in this investigation by a more compact apparatus. The surface of the reaction chamber has been decreased to a minimum. The evacuation of the system at least twice at an interval of twelve hours or more before a run was begun aided the removal of adsorbed gases. In System 3, when the tip was broken from the bulb containing the gas which had been generated, all but about one-fourth of one per cent. immediately dissolved in the standard acid.

4. The error due to the vapor pressure of the mercury where it was used as a confining liquid was eliminated by subtracting the vapor pressure of mercury from the total pressures read for the various temperatures.

5. The errors in the measurement of temperature are very small. The electromotive force measurements may be made with a high degree of precision. By means of a curve constructed for this particular thermocouple from the melting points of Bureau of Standards samples of metals, the electromotive force measurements may be very accurately converted to temperatures. The greatest errors in temperature measurements will not exceed 0.1".

6. The error due to the small changes in the temperature of the furnace is more important, The furnace temperature can be maintained within

0.5°, which corresponds to a maximum error of about 7% in the case of $MgNH_4PO_4{\cdot}6H_2O$ at the lower temperatures where 1° is the equivalent of

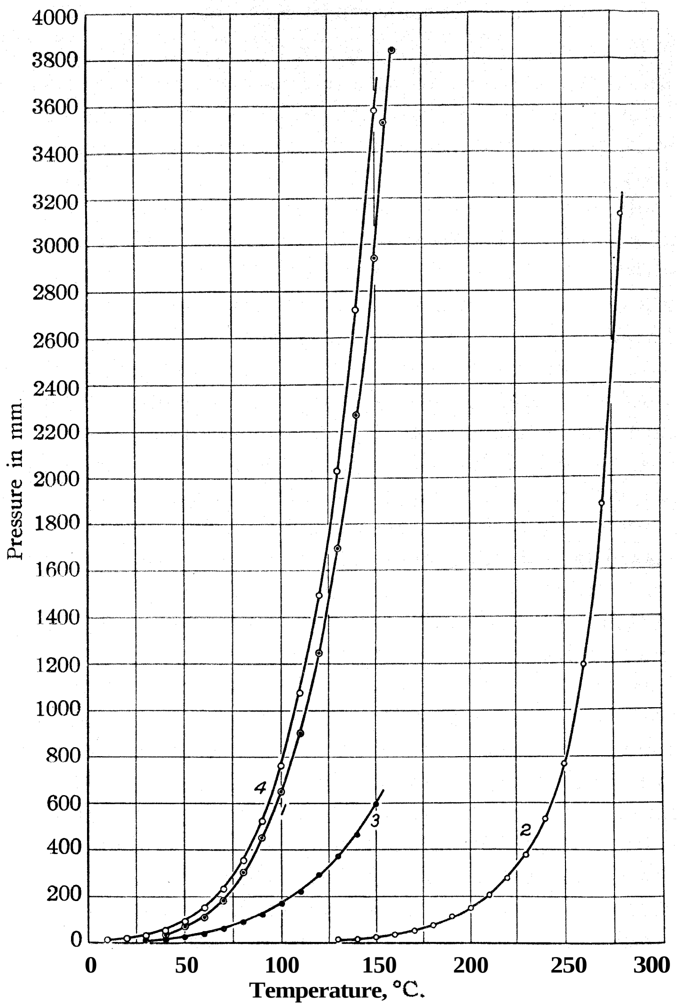

Fig. 2.—The dissociation pressure curves from data in Table IV.

Curve 1. $MgNH_4PO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, H_2O (below 60°) System 1; $MgNH_4PO_4\,6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, $MgHPO_4{\cdot}3H_2O$, H_2O, NH_3 (above 60°), System 2.

Curve 2. $MgNH_4PO_4\,H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O.

Curve 3. $MgHPO_4\,3H_2O$, $MgHPO_4\,H_2O$, H_2O; and the aqueous tension curve for the system.

Curve 4. Liquid water, water vapor.

about 7 mm. and the total pressure is about 50 mm. For the exceptionally high dissociation pressures, as of $MgNH_4PO_4{\cdot}6H_2O$ at 150°, a 0.5' error will cause a pressure error of 50 mm., which, however, in a total pressure of 3400 mm., is only one and one-half per cent.

Discussion of Results

The dissociation pressures obtained in this report show that magnesium ammonium phosphate hexahydrate will lose five molecules of water at a very low temperature when heated. Below sixty degrees no ammonia is noticeable in the gaseous phase. The system is univariant and may be expressed by two components. Above sixty degrees, moreover, the ammonium salt has reached an appreciable dissociation which produces another phase while the system still has one degree of freedom. There are consequently two effects, the dissociation of the hexahydrate and the dissociation of the ammonium salt, one superimposed gradually upon the other. Three components are necessary, therefore, to express the system. Data in Table I and Curve 1 in Fig. 2 are the combined results of the systems studied as 1 and 2, both of which are feasibly reversible over the temperature interval investigated. The dissociation pressure of the substance is but slightly below the aqueous tension of water within this temperature range, and it is equal to one atmosphere at 105°. This explains the formation of the monohydrate when magnesium ammonium phosphate is precipitated from boiling solution. The hexahydrate is stable at lower temperatures only. The fact that the dissociation pressure of the hexahydrate reaches a value of 3834 millimeters or over five atmospheres at 159.1° indicates its unstable character.

The dissociation pressures also show that the monohydrate will lose both its water of hydration and its ammonia in an open vessel when it is heated even considerably below 250°, where it reaches the total pressure of one atmosphere. The vapor phase at this temperature consists of approximately three-fourths water vapor and one-fourth ammonia by volume, and equilibrium is quickly established under the prevailing conditions.

In the study of System 3 it was found that in the heating of $MgNH_4PO_4 \cdot H_2O$, magnesium pyrophosphate was formed whenever both water and ammonia were liberated as gases. This indicates that the water vapor pressure due to the loss of water of constitution by magnesium acid phosphate exceeds that due to the loss of water of hydration by magnesium ammonium phosphate monohydrate when both water and ammonia appear in the gaseous phase. Therefore, if $MgHPO_4$ ever should be formed it would dissociate into water and $Mg_2P_2O_7$. Thus another dissociation is gradually superimposed upon both the dissociation of the hydrate and the dissociation of the ammonium salt.

An epitome of the foregoing facts may be given by the following well-known equation, $2MgNH_4PO_4 \cdot 6H_2O \longrightarrow Mg_2P_2O_7 + 13H_2O + 2NH_3$, which summarizes what takes place when the substance is heated to a temperature which need not exceed 250°, in an open vessel where the gases formed escape as liberated. The equilibrium was found to be attained rapidly near 250°. The speed of the reaction therefore when required to proceed in one direction would be sufficiently great to ensure complete expulsion of the volatile substances in a reasonable time.

In System 2 the reaction is quickly and completely reversible up to about 157°, consisting simply of the two hydrates in equilibrium with water vapor. Above 157° the pressure increases in a very rapid and irregular way and the reaction is not feasibly reversible. Pure $MgHPO_4 \cdot 3H_2O$ which has been heated in the reaction vessel to 158° or more gives a positive test for pyrophosphate with zinc acetate reagent,[5] while that kept below this temperature shows no trace of it.

In System **3** the reaction is completely reversible, although extremely slow. Pyrophosphate appears at a very low temperature, at 200° or less. Here, however, the pyrophosphate seems to convert back to orthophosphate much more readily than in a similar situation in System **5**, whose reversibility was found non-feasible when temperatures were reached where pyrophosphate was formed.

The dissociation of System 4, $MgHPO_4 \cdot 7H_2O$, is especially interesting. When freshly prepared, the crystals were exceptionally large and perfectly formed. However, in a day or two, droplets of water appeared on the walls of the glass-stoppered bottle in which the salt was stored. As the long crystals disappeared, the trihydrate, the stable phase, was formed.

It was found, moreover, that the pure heptahydrate, when once inoculated with the trihydrate and evacuated in the pressure–temperature apparatus, formed liquid water in five minutes or less at any temperature from room temperature to at least 100°. The crystals, still in the water from which they were precipitated, left standing on the shelf, also changed completely into the trihydrate at the same temperature at which precipitation took place (about 22°) in about one week. This change, furthermore, was greatly promoted by light. When the pure heptahydrate decomposed, moisture condensed on that side only of the bottle which was turned toward the light. A sample of it, on the other hand, in a glass-stoppered bottle wrapped in a black cloth required a much longer time to change completely into the lower hydrate than an identical unprotected sample standing beside it. It may be concluded, therefore, that magnesium acid phosphate heptahydrate, at room temperature, has a dissociation pressure as great as or greater than the aqueous tension of liquid water.

Summary

1. A modified apparatus is described for measuring the dissociation pressures of substances that give both water and another condensable gaseous substance.

2. A method is given for measuring and for resolving into partial pressures the dissociation pressures of salt hydrates, where both water and

another gaseous substance are produced, and where the total measured pressure may be high.

3. The dissociation pressures for the systems

$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O (below 60°)
$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3 (above 60°)
$MgNH_4PO_4 H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O
$MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, Hz0

have been determined.

4. The use of Wood's metal as a confining liquid is described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Lead–Mercurous Acetate Voltaic Cell with Acetic Acid as the Solvent[1]

BY GRADY TARBUTTON AND WARREN C. VOSBURGH

The reproducibility that has been attained in the preparation of voltaic cells with non-aqueous electrolytes is in general less than that of cells with aqueous electrolytes. Among those who have attained a reproducibility of within a few tenths of a millivolt are Brodsky,[2] Afanasiew,[3] Isaacs and Partington,[4] and Harned and Fleysher,[5] all with alcoholic electrolytes, and Yoshida,[6] who set up cadmium–mercurous iodide cells with water, methanol, ethanol, propanol and acetone as solvents. The electromotive forces in most other investigations with non-aqueous electrolytes have been reported only to the nearest millivolt.

It seemed worth while to test the reproducibility of cells with acetic acid as the electrolyte solvent. Hutchison and Chandlee[7] have prepared a series of hydrogen–mercurous sulfate cells with acetic acid as the solvent, but the difficulty of either excluding water entirely or keeping its concentration very constant was involved. The cell chosen for this work was a lead–mercurous acetate cell, which when pure acetic acid is the solvent can be represented as follows

$$Pb(Hg) \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2 \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2, Hg_2(C_2H_3O_2)_2 \mid Hg$$

Materials and Apparatus.—The purification of the acetic acid and of the lead acetate are described in an earlier paper.[8] Mercurous acetate was

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[1] Part of a thesis submitted by Grady Tarbutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1932.

[2] Brodsky, *Z. physik. Chem.*. **121**, 9 (1926).

[3] Afanasiew, *Z. Elektrochem.*, **35**, 221 (1929).

[4] Isaacs and Partington, *Trans. Faraday Soc.*, 25, 56 (1929).

[5] Harned and Fleysher, THIS JOURNAL, 47, 82 (1925)

[6] Yoshida, *Chem. Abs.*, **22**, 1893 (1928).

[7] Hutchison and Chandlee, Tars JOURNAL, **53**, 2884 (1931)

[8] Tarbutton and Vosburgh, *ibid.*, 54, 4537 (1932)

prepared by precipitation and lead amalgam electrolytically, both **from** purified materials.

An oil-bath was used for temperature control. At 25° fluctuations in temperature were not more **than** ±0.01°, but at other temperatures about ±0.02'. Temperatures were measured to within ±0.02".

Electromotive force measurements were made as described by Vosburgh and Elmore.[9]

The cell vessels used were of the "H" form of the sizes given below. For the earlier cells vessel 1 was used. Later, on account of low conductance, vessel 2 was used.

No.	Length, cm.	Width, cm.	Cross arm to base, cm.	Diameter of tube, cm.
1	17	4.7	9	1.1
2	14.8	5.5	4	1.8

Preparation of **the** Cells.—A lead acetate solution was prepared by adding an excess of lead acetate to acetic acid or a mixture of acetic acid and water. The solution was saturated either by mechanical shaking or by heating until the solid was dissolved and then seeding with the proper crystal form.[10] The latter procedure is preferable. By the former the wrong crystal form was introduced into some of the cells, which made considerable delay in the attainment of equilibrium. The solution so prepared is designated below as solution 1. A sample of solution 1 saturated at a definite temperature, usually 30°, was analyzed by the methods previously described. Previous to introducing into the cells, dissolved air was removed from solution 1.

A portion of solution 1 was saturated with mercurous acetate, giving solution 2.

The empty cell vessel, which had been properly cleaned, was placed in a beaker of water at about 75°. Lead amalgam, heated to dissolve the solid phase, was placed in one leg of the vessel, covered with a little of solution 1 and allowed to cool slowly to room temperature along with the water in the beaker. It was shown that rapid cooling gave an amalgam of higher lead activity than slow cooling, and that the difference might amount to over 0.1 mv. By slow cooling, amalgam reproducible to less than 0.01 mv. could be obtained.

The amalgam when cool was washed three times with solution 1. Then a portion of the excess solid lead acetate in equilibrium with solution 1 was placed above the amalgam to form a thick layer. This was covered with solution 1.

Mercury was then placed in the other leg of the vessel and washed three times with solution 2.

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(9) Vosburgh and Elmore, THIS JOURNAL, 63, 2822 (1931).

(10) See Ref. 8, p. 4539.

Some mercurous acetate was filtered by suction from the solution under which it was kept and washed with solution 2. It was transferred to an agate mortar and mixed well with about a fourth of its volume of lead acetate crystals (some of the excess solid from solution 1) and some solution 2. The paste was then washed three times by decantation with solution 2. A layer of this paste about one centimeter thick was placed above the mercury in the cell vessel.

A thick layer of lead acetate crystals (some of the excess solid from solution 1) was placed above the mercurous acetate paste and enough solution 1 added to fill the vessel to a point above the cross-arm. The upper part of the vessel was flushed out with nitrogen and stoppered with paraffined corks. On top of the corks was poured molten sealing wax or ceresin wax. All cells were made in duplicate.

Electromotive Force Measurements.—It has been shown that three different solid phases can exist in equilibrium with saturated solutions of lead acetate in acetic acid–water mixtures. The cells can be divided into three groups, each group containing a particular solid phase. The electromotive forces over a period of several months are given in Tables I, II and III.

TABLE I

CELLS WITH $Pb(C_2H_3O_2)\cdot 3H_2O$ AS THE SOLID PHASE

Cells	$HC_2H_3O_2/H_2O$[a] ratio by wt.	Electromotive force at 25° 7 Days v.	1 Month v.	6 v.	12–14 v.	15–18 v.
12, 13, 16	0.1969	0.74715	....	0.74729	0.74708	0.74709
17, 18	0.4757	....	0.74480	.74463	.74462	,74462
19, 20	1.144	.73938	.73945	,73921	.73924	....
21, 22	1.552	.73491	.73497	.73444	....	....

[a] The samples analyzed were saturated with lead acetate at 30°. At 25° the ratio would be somewhat larger.

Many of the cells decreased 0.2 to 0.5 mv. between the first and sixth months, but were nearly constant after the sixth month. That the decrease is not continuous is an indication that it is the result of faults of technique. A continuous change might be the result of reaction of the acetic acid with the lead of the amalgam or diffusion of the appreciably soluble mercurous acetate to the amalgam and its reaction with the lead. No evolution of hydrogen at the amalgam was observed. The conductance was sufficient for measuring the electromotive forces to 0.01 mv. The average difference between duplicate cells was 0.07 mv.

Cells 23–26 of Table II decreased appreciably in electromotive force over a period of a year. They may have contained some of the wrong solid phase at the beginning. Cells 38–39 increased. The others changed only a little. Improvements in technique, especially the method of preparing the solutions, were probably responsible for the better results in cells 44–47. The average difference between duplicates omitting cells 25–26 was 0.04 mv.

TABLE II

CELLS WITH $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ AS THE SOLID PHASE

Cells	$HC_2H_3O_2/H_2O$ ratio by wt.	Electromotive force at 25° 7 Days v.	1 Month v.	4–6 v.	10–12 v.
38, 39	3.886[a]	0.72846[c]	0.72851"	0.72877	0.72883
23, 24	4.715"	.72807	.72802	.72792	.72767
25, 26	4.932"	.72940	.72897	.72852	.72832
34	5.617[a]	.72772[c]	.72744[c]	,72760	.72763
46, 47	6.746'	.72632	.72632	.72623	....
44, 45	7,730[b]	.72609	.7261	.72614	....

[a] The samples analyzed were saturated at 30°. [b] The samples analyzed were saturated at 25°. [c] Calculated from measurements at 30°.

The solubility of lead acetate was large in the range of the cells of Table II. The solutions were quite viscous, and the conductance was such in some cases that it was difficult to read the electromotive force to better than 0.1 mv. The use of the larger cell vessels helped in this respect.

It can be seen that the electromotive force changes quite appreciably with change in the ratio of acetic acid to water in the electrolyte. This shows that the solid phase is a solvated compound, in agreement with the analytical data presented in the earlier paper.

TABLE III

CELLS WITH $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ AS THE SOLID PHASE

Cells	$HC_2H_3O_2/H_2O$ ratio by wt., 25°	Electromotive force at 25° 7 Days v.	1 Month v.	3 v.	6 v.
42	10	0.7268	0.7270	0.7272	0.7272
43	10	.7271	.7270	.7272	.7272
40	26	.7216[a]	.7279	.7279	.7279
41	26	.7216[a]	.7279	.7279	.7279
48	90[b]	.72902	.72903	.72900	...
49	90[b]	.72908	.72903	.72902	...
54	..[c]	.72895[d]	.72864[d]	.72908	...
55	..[c]	.72895[d]	.72866[d]	.72908	...

[a] These cells had fine needle-like crystals when prepared. After a week the cells were opened and seeded with the stable solvated crystals. The solid phase began to change over immediately, and the electromotive force became constant within a few hours. [b] The solution was nearly anhydrous; the ratio is subject to considerable error of method. [c] The solution was made to duplicate that of cells 48–49, but was not analyzed. [d] Calculated from measurements at 30°.

With regard to constancy and reproducibility the cells of Table III were the most satisfactory yet considered. Cells 42–43 were not as good as the others at first, but became constant later. Cells 40–43 had so much solid phase in them that the resistance was high and the electromotive force could not be measured to better than ±0.05 mv. Cells 48–49 and 54–55 had not as much solid phase and could be measured more precisely.

The change in electromotive force with composition again shows that the solid phase is solvated. As the water content decreases, the solubility of lead acetate decreases rapidly, and the mole fraction of acetic acid increases. The increase in electromotive force with increase in mole fraction of acetic acid would be expected if the solid phase is an acetic acid solvate, because in this case acetic acid is one of the reactants in the cell reaction. The cell data again confirm the solubility results previously reported.

The electromotive force of cells **4041** after seven days is of interest. These cells contained a solid phase obtained by spontaneous crystallization from a supersaturated solution. It consisted of fine needle-like crystals. The electromotive force after seven days is nearly in agreement with that of an earlier pair of cells, which was **0.72166** and **0.72173** v., respectively. These latter cells were made with an electrolyte containing quite a bit of water and with dehydrated lead acetate as the solid phase. The constant electromotive force with the different composition in the two pairs indicates that both had the unsolvated salt as the solid phase.

The unsolvated lead acetate of cells 40–41 changed over to the solvated form on being seeded, and the electromotive force increased. The electromotive force of the earlier cells increased slowly without seeding.

While the electromotive force is dependent on the composition of the solution in all the cells having stable solid phases, it should be noted that at the transition points the composition is fixed when both solid phases are present. Eight cells were made with the two hydrated solid phases in equilibrium with the saturated solution. The solutions did not have the composition of the transition point when first prepared but approached it gradually after the cells were set up. The cells were not constant at first and did not agree until constancy was attained.

TABLE IV

CELLS WITH BOTH $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ AND $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ AS SOLID PHASES, 25°

Cells	Initial v.	7 Days v.	1 Month v.	6 v.	12 v.
27	*0.72994*	*0.72974*	*0.73002*	*0.73033*	*0.73031*
28	.72994	.72922	.72956	.73018	.73032
36	.72929[a]	.72992[a]	.73011[a]	....	....
37	.72937[a]	.73001[a]	.73019[a]	.73018	.73017
50	.73098	,73055	.73015	....	....
51	.73068	.73047	.73017	....	....
52	.73088[a]	.73078[a]	.73072[a]	.73044[b]	....
53	.73090[a]	.73078[a]	.73073[a]	.73044[b]	....

[a] Calculated from measurement at 30°. [b] Three months.

It can be considered that the reaction for the cells of Table IV does not involve the electrolyte. The anhydrous lead acetate produced by reaction of lead with mercurous acetate must become hydrated at the expense of the trihydrate present, since the composition of the solution cannot change. The reaction, therefore, is

$$5\text{Pb(amalgam)} + 5\text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{H}_2\text{O} \longrightarrow 6\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 0.5\text{H}_2\text{O} + 10\text{Hg} \quad (1)$$

The change of electromotive force with temperature was therefore determined in order to calculate the heat of reaction.

TABLE V

CHANGE OF ELECTROMOTIVE FORCE WITH TEMPERATURE

	$E_t - E_{25}$						
Cells	t = 16° mv.	20° mv.	30° mv.	35° mv.	40° mv.	45° mv.	50° mv.
27–28	−1.02	−0.59	0.20	0.50	0.77	0.97	0.76
36–37	−0.63	− .18	.20	.53	.70	0.82	.91
Calcd.	− .45	− .25	.25	.50	.75	1.00	. .

The variation with temperature is linear within the limits of error and follows the relationship

$$E_t = E_{25} + 0.000050(t - 25)$$

as shown in the table.

For the cell Pb(Solid)/Pb^{++}/Pb(Hg) Gerke[11] found the value $E = 0.0057 + 0.000016\ (t - 25)$. Combining the two cells gives the electromotive force of the lead–mercurous acetate cell with a solid lead electrode, of which the electromotive force is $E = 0.7359 + 0.000066\ (t - 25)$. Application of the Gibbs–Helmholtz equation gives $\Delta H = -165.26$ kg. cal. with an uncertainty of not more than 0.2 kg. cal. If this is substituted in Equation 1 along with the values for the heats of formation of lead acetate trihydrate and mercurous acetate, namely, 446.12 and 203.34 kg. cal., respectively,[12] the heat of formation of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 0.5\text{H}_2\text{O}$ is found to be 271.35 kg. cal. The precision of this value depends mainly on that of the heats of formation of lead acetate trihydrate and mercurous acetate.

The temperature coefficients of the other cells were determined also. The cells with the higher water concentrations had negative temperature coefficients. The temperature coefficient approached zero as the ratio of acetic acid to water increased, and was positive for the cells with the higher ratios. It is interesting to note that a cell with the trihydrate as the solid phase and a ratio of acetic acid to water a little larger than that of cells 21–22 should have a zero temperature coefficient.

In connection with the temperature coefficient measurements, during which the cells were heated to 52°, no tendency of any of the solid phases to change to a more stable form was noted.

Summary

Lead–mercurous acetate voltaic cells have been set up with solvents covering a wide range of acetic acid–water mixtures and including nearly anhydrous acetic acid, and with three different solid phases.

[11] Gerke, THIS JOURNAL, 44, 1684 (1922).

[12] "International Critical Tables," Vol. V, pp. 184, 187

Duplicate cells with nearly pure acetic acid as the solvent could be reproduced to within 0.1 mv. and were constant in electromotive force for several months at least.

A cell containing two solid phases in equilibrium with the saturated solution was prepared.

The heat of formation of the compound $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ was determined.

DURHAM. NORTH CAROLINA

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions as a Function of the Concentration

BY GRINNELL JONES AND SAMUEL K. TALLEY

It has long been known that the viscosity of aqueous solutions is approximately a linear function of the concentration. In 1876 Sprung[1] published measurements on many salts at many temperatures. His viscosity–concentration curves are approximately linear but have an upward trend at higher concentrations which indicates an increasing deviation from a linear limiting law. Arrhenius[2] also found that the linear relationship holds approximately over the lower part of the concentration range but that the viscosity increases more rapidly than the concentration at high concentrations. He proposed an equation which is reducible to the form $\eta = A^c$, η is the relative viscosity compared to that of water at the same temperature and A is an empirical constant for any salt and temperature. This equation has been much used by later experimenters although it is only a rough approximation.

Most salts give solutions with viscosity greater than that of water at all concentrations. Some salts (including most but not all of the iodides, bromides, chlorides, bromates, chlorates, nitrates and thiocyanides, of cesium, rubidium, potassium, ammonium, thallium and hydrogen) give solutions having a viscosity less than that of water.[3] In such cases it is usual for the viscosity–concentration curve to go through a minimum and for some salts at sufficiently high concentrations the viscosity may become greater than that of water. This type of curve cannot be reproduced by the Arrhenius equation.

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(1) A. Sprung, *Pogg. Ann Phys Chem.*, *159*, 1 (1876)

(2) S. Arrhenius, Z. *physik. Chem* , *1*, 285 (1887).

(3) A. I. Rabinovich, THIS JOURNAL, 44. 954 (1922), discusses the hypotheses which have been suggested to account for this phenomenon An interesting suggestion has recently been made by Z. W. Wolkowa and W. S. Titow [*Z. physik. Chem* , **A155**, 53 (1931)], who say "We may therefore suspect (vermuten) that an aqueous solution can only have a greater fluidity than water if the heat of dilution is negative."

Einstein[4] in **1906** deduced from the principles of hydrodynamics that if the solute could be regarded as made up of spherical incompressible uncharged particles which are large in comparison with the molecules of the water the viscosity of the solution would be $\eta = 1 + 2.5\,\Theta$, where Θ is the total volume of the solute particles per unit volume of solution. This equation obviously connotes a linear relationship between viscosity and concentration.

Finkelstein[5] extended Einstein's treatment to solutions of binary electrolytes in polar solvents. He investigated mathematically the effect on the viscosity of the relaxation time of the solvent dipoles and concluded that the electric influence of the ions on the polar solvent will increase the viscosity proportionally to the concentration. Neither Einstein nor Finkelstein account for the fact that some solutes diminish the viscosity of water.

Grüneisen,[6] who improved the experimental technique and extended his measurements to greater dilution than his predecessors, found that for sucrose the linear relationship is valid; but that for salts, deviations from the linear law became more pronounced at low concentrations instead of disappearing. Griineisen made the deviation from linearity evident by plotting $(\eta - 1)/c$ against c (or some root of c for the sake of spreading out the points at the lower concentrations). This method of plotting would give a horizontal straight line if the linear relationship held. His curves, however, show a pronounced negative slope at low concentrations, pass through a minimum at about **0.2** normal and then have a slight positive slope and positive curvature at higher concentrations. We shall call the departure of the viscosity–concentration curves from linearity at high dilutions the Griineisen effect. However, Griineisen's attempts to give a theoretical explanation of the failure of the linear law at high dilutions, on the basis of Arrhenius' theory of electrolytic dissociation, and to derive an equation expressing the viscosity as a function of the concentration were unsuccessful.

Later workers, especially Schneider, Applebey and Merton,[7] found the Grüneisen effect with other salts, but they did not give a satisfactory interpretation or derive a valid equation for the variation of the viscosity with the concentration.

Measurements of the viscosity of solutions of barium chloride were undertaken in this Laboratory by the senior author and Malcolm Dole[8] on account of their interest in these data in connection with the phenomena

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(4) A. Einstein, *Ann. Physik*, [4] 19, 289 (1906): [4] 34, 591 (1911).

(5) B. N Finkelstein, *Physik. Z.*, 31, 130, 165 (1930).

(6) E. Gruneisen, *Wiss. Abhandl. physik. tech Reichsanstalt*, 4,151, 237 (1905).

(7) K. Schneider, "Dissertation," Rostock, 1910, M P Applebey, *J. Chem Soc.*, *97*, 2000 (1910); T. R Merton, *ibid.*, 97, 2454 (1910).

(8) Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 2950 (1929). This paper contains a more detailed discussion of the Gruneisen effect

of electrolytic conductance and for this purpose were carried to a high dilution (0.005 molal). These measurements showed that the Grüneisen effect is magnified at great dilution. Analysis showed that in this case the fluidity-concentration curve has a simpler form than the viscosity–concentration curve. It was pointed out that, although the principal effect of the dissolved salts on viscosity is proportional to the concentration, the curvature (discovered by Grüneisen) in the dilute end of the viscosity–concentration (or fluidity–concentration) curves proves that there is another effect of the dissolved salt which is of relatively greater importance in dilute solutions. The Grüneisen effect always tends to increase the viscosity regardless of whether the sum of all of the effects of the salts is to increase or decrease the viscosity.

It then occurred to Jones and Dole that the Debye–Hückel theory of interionic attraction might be extended by applying it to this problem. The electric forces between the ions tend to establish and maintain a preferred arrangement of the ions and resist any distortion of the preferred arrangement and thus stiffen the solution or increase its viscosity. Although they did not succeed in deriving an equation for the viscosity as a function of the concentration which makes adequate allowance for the Grüneisen effect by rigid deduction from fundamental postulates of the Debye–Hückel theory, they inferred that the effect would be proportional to the square root of the concentration. This idea together with the knowledge that, for salts which increase the viscosity of water, the fluidity is approximately a linear function of the concentration suggested an equation of the form $\varphi = 1 + A\sqrt{c} + Bc$; where φ is the fluidity (*i. e.*, the reciprocal of the relative viscosity) and A would be expected to be negative for all electrolytes but zero for non-electrolytes. The value of B may be either positive or negative in different cases. The equation $\varphi = 1 - 0.02013\sqrt{c} - 0.20087\,c$, was found to fit their data for barium chloride over the whole range from 0.005 to 1 molal. It was furthermore found that the equation is consistent with the best data on other salts available in the literature, although the scarcity of precise measurements at low concentrations hindered a rigid test of the general validity of the equation.

The manuscript of the paper by Jones and Dole was then taken to Debye by Dole during the summer of 1929. Debye suggested that the problem could be attacked by modifying the fundamental differential equation of Onsager to allow for the viscous flow. With the inspiration of Debye's interest and suggestions, Falkenhagen and Dole[9] then attacked the problem deductively and found a partial solution. In order to simplify the problem it was at first assumed that only a binary salt is present and that the anion and the cation have the same mobility. The result was an equation,

(9) H Falkenhagen and M Dole, *Z physik. Chem.*, [B] 6, 159 (1929); *Physik. Z.*, 30, 611 (1929)

$\eta = 1 + A\sqrt{c}$, which was, however, regarded only as a limiting law for extreme dilution. It is obvious that A in this equation is the same as the A in the Jones and Dole fluidity equation with a reversed sign. Later the mathematical difficulties of a more general treatment were overcome by Falkenhagen,[10] who derived an equation of the same form, but with a more explicit evaluation of the coefficient A, applicable to any salt with ions of any valence and any mobility.

The deductive treatment of Falkenhagen is a substantial advance over the inductive treatment of Jones and Dole in that the coefficient A is given as a complicated but explicit function of the mobilities and valences of the ions, the temperature, and the universal constants which commonly appear in the equations derived from the Debye-Hückel theory. Falkenhagen and Vernon have computed the value of A for a number of salts. However, the deductive reasoning of Falkenhagen did not give the linear term, which is numerically greater than the square root term except at extreme dilutions. On the other hand, the inductive reasoning of Jones and Dole has given a new law for the relationship of viscosity to concentration which appears to be valid over a substantial range of concentration.

The original paper of Jones and Dole contains the following statement: "It may be predicted from our equation that at very low concentrations the viscosity of solutions of all strong electrolytes will be greater than that of water, including salts which at moderate concentrations show diminished viscosity. So far as we are aware, the only published measurement which shows that even those salts which cause diminished viscosity at moderate concentrations will give an increase in viscosity at extreme dilutions is by Schneider, who reports a relative viscosity of 1.0008 for 0.05 *N* potassium chlorate, and a viscosity of less than 1 for solutions of 0.1 to 0.5 *N* potassium chlorate. We expect to test this prediction experimentally in the near future."

Schneider makes no comment on the significance of his recorded observation that 0.05 *N* potassium chlorate has a viscosity greater than 1 whereas stronger solutions have a viscosity less than that of water.

Since the publication of the prediction by Jones and Dole quoted above, Joy and Wolfenden[11] have tested this prediction by means of new data on potassium chloride, rubidium nitrate, potassium chlorate, and nitric acid at both 18 and 35°. They have confirmed the prediction for the three salts at 18° and for rubidium nitrate at 35°, but have found that nitric acid increases the viscosity at all concentrations at both of these temperatures, and potassium chloride and chlorate behave likewise at 35°. Incidentally they found that Schneider's figure of 1.0008 for the viscosity

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(10) H. *Falkenhagen,* Physik. *Z.,* 32, 365, 745 (1931); *H. Falkenhagen and E. L* Vernon, *ibid*, 33, 140 (1932); *Phil. Mag.,* [7] *14,* 537 (1932)

(11) W. E. *Joy and J. H. Wolfenden, Nature,* 126, 994 (1930); *Proc. Roy. Soc.,* A134, 413 (1931); H. *G.* Smith, J *H. Wolfenden and* Hartley, *J Chem Soc.,* 403 (1931); G. R. *Hood, J. Rheology,* 3, 326 (1932).

of 0.05 N potassium chlorate at 18° is an experimental error. Their measurements show that at this concentration and temperature the viscosity is really less than that of water and that a viscosity greater than that of water is only found at concentrations less than 0.008 N.

The primary object of the present investigation was to test the validity of the prediction of Jones and Dole that all salts will give solutions which have a viscosity greater than that of water if measured at sufficiently great dilution, even including those salts whose solutions exhibit diminished viscosity at moderate concentrations. Secondary objects were to collect additional data to test the general validity of the Jones and Dole equation, to compare the values of A found experimentally with the value computed by the formula of Falkenhagen and Vernon, and to test more rigorously the conclusion drawn from existing data that the square root term is absent for non-electrolytes.

In order to accomplish our primary object it was evidently necessary to measure the relative viscosity of extremely dilute solutions with high precision. The analysis of the meager existing data on salts which give solutions having a viscosity less than that of water indicated that the maximum in the viscosity–concentration curves would probably be less than 0.1% greater than that of water. Therefore data reliable to 0.01% or better are needed.

The earlier measurements on viscosity in this Laboratory had been carried out by observing the movement of a meniscus past a mark on the viscometer and tapping a key with the hand to record the instant of transit on the moving tape of a chronograph. Our experience with this method made it clear that the greatest source of error was that due to an inexact coordination of the eye and hand. We therefore undertook to eliminate this psychological error entirely by substituting a photoelectric cell and its amplifier and other accessories for the human eye, brain, nerves and hand, in the hope that a more precise record of the time of transit of the meniscus in the viscometer could be obtained.

Experimental

A new viscometer of quartz of the Ostwald type was made for this investigation at the Lynn Works of the General Electric Company. The workmanship is extraordinarily good and our exacting specifications were met with astonishing precision. It is shown in Fig. 1.

In order to avoid any surface irregularities which might cause irregular drainage the tube from which the bulb, B, was made was ground and polished internally before being drawn down and sealed to the tubes C_1 and C_2. Care was taken that the end portions of the bulb connecting the side walls of the bulb and the constriction should have sufficiently steep slopes at all points to give good drainage over the entire surface.

The time of flow was determined by timing the transit of the meniscus past fixed points in the upper and lower constrictions C_1 and C_2. The diameter of these tubes is an important detail. By making them narrow the rate of motion of the meniscus is increased and therefore the event to be timed is made more definite. On the other hand, if the tube C_1 is made too narrow the liquid draining from the upper wall after the passage of the meniscus will bridge across the tube and will obstruct the entrance of air into the bulb. Of course this obstruction will soon be broken by the suction of the receding liquid, but the drop of liquid will immediately be drawn back into the capillary tube by its surface tension. This process repeats itself indefinitely. The result is an extra irregular back pressure which gives erratic and erroneous results. The tube C_1 must, therefore, be wide enough to remain free of drops after the meniscus has passed. After some preliminary trials with tubes of various diameters we specified a diameter of 10 mm. for this tube with satisfactory results. The lower tube C_2 should be of the same diameter so that the two transits which are to be timed shall be as nearly identical as possible. The tubes C_1 and C_2 were therefore made from the same piece of tubing. The ground joints connecting the upper Pyrex cross piece with the viscometer were placed on the outside of the viscometer because this construction minimizes the danger that ground glass or grease will get into the viscometer. The more important dimensions are the average hydrostatic head, 22.8 cm.; the volume of the upper bulb, 10.063 ml.; the length of the capillary, 18.5 cm.; the diameter of the capillary, 0.0476 cm. The period with water at 25° is approximately 618 seconds.

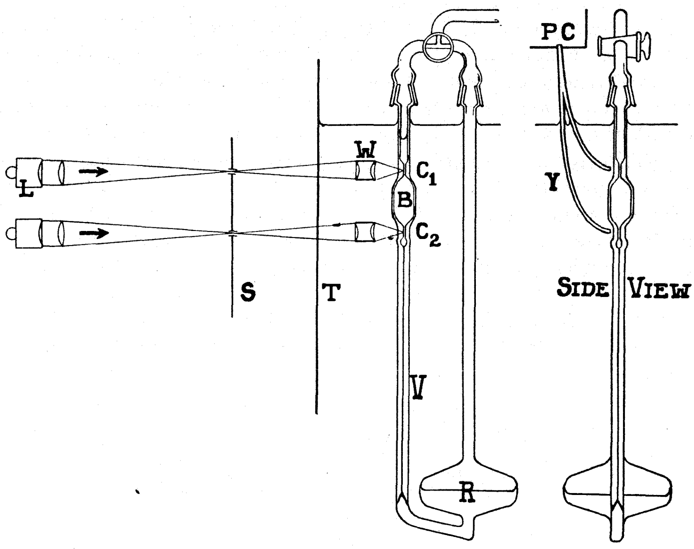

Fig. 1.—Viscometer and optical system.

The viscometer was mounted permanently in a stout brass frame and was always handled in its frame. It is important that after the instrument is removed from the thermostat for cleaning and refilling it shall always be put back in a definite reproducible position so that the hydrostatic head shall be constant. The frame was therefore held at only three points against a strong well-braced support which was designed to give mechanical stability with minimum of interference with the circulation of the water of the thermostat.

Since the viscosity of water changes about 2% per degree, the thermostat used must be of high quality. Our thermostat apparently maintained its temperature within 0.001° but the means used to obtain this constancy need not be described in detail since they are not novel. Our thermostat was set at 25.00° for all of the measurements recorded in this paper. Since the temperature coefficient of a dilute solution will not vary greatly from that of water the absolute value of the temperature does not have to be known with great precision.

The most novel feature of our viscometric procedure was the development and use of automatic timing of the transit of the meniscus by means of a photoelectric cell. The method of timing finally adopted was based on the total internal reflection of a beam of light at the quartz-air interface which is formed in the constriction at the instant of the transit of the meniscus. This method requires a beam of light which is as narrow as possible vertically but broad enough horizontally to cover at least half of the tube C_1 and which can be focused at a definite reproducible height on the tube C_1. The source of light was an automobile head-light bulb (6 candle power, 6 volts) with a straight tungsten filament which was mounted so that the filament would be horizontal. In order to secure more intense illumination the bulb was operated with 10 volts instead of its rated 6 volts. The light passed through a condensing-projecting lens, L (a Bausch and Lomb, series II Cinephor with an effective focal length of five inches and a relative aperture of 3.5) and was brought to a primary focus outside the thermostat, as shown in Fig. 1. A screen with a horizontal slit was placed at this focus. This helped greatly in obtaining a beam which was narrow vertically at the viscometer. The diverging beam from the slit passed through a plate glass window in the side of the thermostat and then through a double lens, W, which brought the beam to a focus on the viscometer at C_1. In order to increase the relative aperture without increasing the aberrations the parts of the final double lens were mounted in a water-tight cell so that their more refractive inner surfaces were in contact with the enclosed air and the outer surfaces were in contact with the water of the thermostat This lens when mounted as described in water had an effective focal length of 75 millimeters and a relative aperture of 2.5. A single lamp and projecting lens, L, served for both the upper and lower meniscus by mounting them in an elevator provided with suitable stops. The final double lenses, W, and slit in the screen, S, were duplicated so that each constriction C_1 and C_2 had its own lens and slit which remained in a fixed position. The double lenses were especially made for us by the firm of Pinkham and Smith of Boston We wish to thank Mr. John A. Seaverns of this firm for his help in the construction of this optical system.

The optical effect which forms the basis of our new method of timing is shown diagrammatically in Fig. 2.

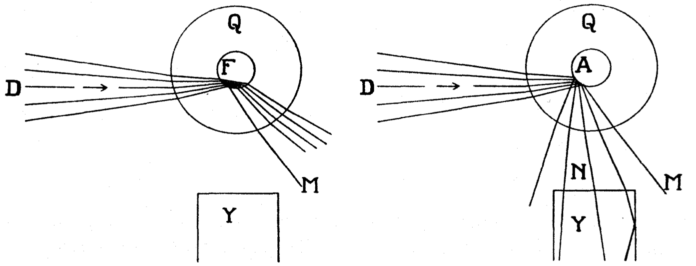

Fig. 2.—Principle of optical effect at meniscus transit.

When the narrow horizontal beam of light, D, strikes the quartz–water interface at the capillary tube inside C_1 most of the light will pass into the water, F, inside the capillary and finally emerge into the water of the thermostat nearly opposite where it entered the quartz. A small portion of the light beam which strikes the interface at a sufficiently acute angle will suffer total internal reflection as shown (M) but will miss the collecting rod of quartz, Y. However, as soon as the meniscus has passed below the light beam the water inside the capillary will be replaced by air, A, and as a consequence the critical angle for total internal reflection will be greatly changed, and therefore a much larger portion of the beam will suffer a total internal reflection to the side as shown at N in Fig. 2 and will emerge from the quartz tube into the water of the thermostat at an angle from the entering beam. The light thus diverted sideways enters the end of a quartz collecting rod, Y, which is suitably mounted near C_1 and C_2, and passes through the rod lengthwise to the photoelectric cell. The light cannot emerge into the water of the thermostat owing to total internal reflection provided the curves in the rod are not too sharp.

The two quartz collecting rods from the two constrictions were joined together in the form of a Y as shown in Fig. 1. The upper end of the quartz rod entered a light-tight box where the photoelectric cell was mounted. The invention of this method of producing a side-wise reflection of the light at the moment of transit of the meniscus and the device of leading this reflected light out of the water of the thermostat to the photoelectric cell by means of a quartz rod are the essential novel features of our method of timing. It was developed only after patient experimentation and adopted after critical comparison with other procedures which proved to be less satisfactory. The development of the rest of the apparatus to record the time accurately, although laborious and expensive, was comparatively speaking a routine matter. We used the photoelectric cell made by the General Electric Company and designated by them as type PJ-23. It is more sensitive than any other cell which we tried. Dr. R. F. Field and Mr. Horatio Lamson of the General Radio Company kindly brought their new type of stretched wire oscillograph to our laboratory and made some measurements on the current given by the photoelectric cell both when using the optical effect described above and when using other effects which proved to be less useful and are therefore not described here. These oscillographic tests showed that, when operating as described above, about 0.05 second was required from the time when the current from the photoelectric cell could be first detected until it reached its maximum value. This presumably measured the total time of transit of the meniscus through the height of the beam of light. This does not mean, however, that there is an error or uncertainty of this magnitude in our final results because the electromagnetic recording device operated when the current attained a definite value less than the maximum. We are measuring the difference in time between two very similar transits and the recording device operated at the corresponding stage of the two transits and thus gave the interval correctly. Moreover, we always compared the time of flow of a dilute solution with that of water so that any constant errors would be canceled out of the results.

The power output from a photoelectric cell is too small to operate the chronograph needle directly and must therefore be amplified. There are difficulties in amplifying a current which takes 0.05 second to build up from zero to its maximum, which corresponds to a frequency of 5 cycles per second, but they can be overcome. The amplifier finally built uses three audion tubes with resistance–capacitance coupling and a minimum of inductance. It is shown diagrammatically in Fig. 3. The types of tubes and the voltages used are shown in the figure. The best values for the resistances and capacitances indicated in the diagram will depend to some extent on the individual tubes. In our apparatus R_1 was 20 megohms, R_2 and R_4 were each 2 megohms, and R_3 and R_5 were 1 megohm each, C_1 and C_2 were 2 microfarads. When the meniscus transit occurs the electric impulse from the amplifier through the chronograph was about 20 milliamperes. The photoelectric cell and entire amplifier, except the batteries, was contained in an electrostatically shielded box mounted immediately over the thermostat. We do not claim that this amplifier is the best possible design but merely that it worked satisfactorily. Figure 3 also shows a switch, CK, which when closed connected the clock to the chronograph and recorded seconds on the tape; and a tapping key, IK, which permitted the operator to make a mark on the tape at will to identify or call attention to any particular signal from the clock or photoelectric cell.

Our timing depended on a pendulum clock of good quality made by the Gaertner Scientific Company of Chicago and described in their catalog under Number *L1013*. The invar pendulum carried a platinum tip which swung through a small trough of mercury, thus closing, once every second, an electric circuit including a battery and the chronograph. It seems improbable that the rate of this clock varied sufficiently during any day to cause an error of 0.01 second in 618 seconds.

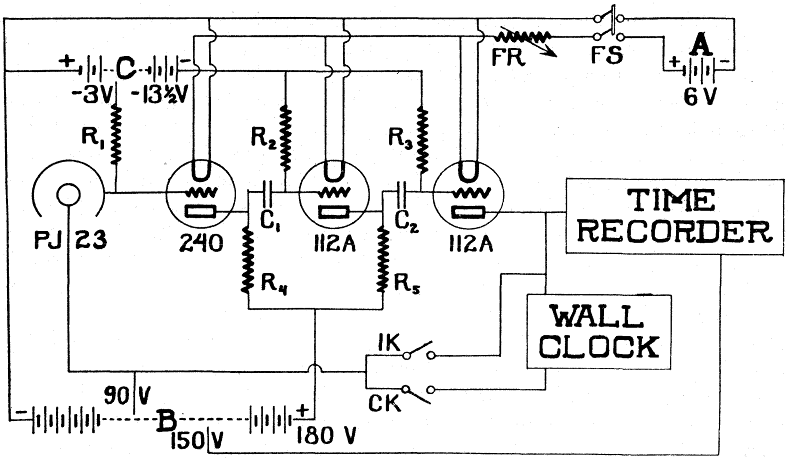

Fig. 3.—Photoelectric cell, amplifier and electrical connections

The chronograph used was a Duplex Syphon Recorder made by the General Radio Company of Cambridge and designated by them as type 456. It had a moving paper tape (stock market ticker tape) which had an idling speed of 2.5 cm. per second and a recording speed of 30 cm. per second. It had two independent siphon pens operated by electromagnets which required about 5 milliamperes more or less dependent on the adjustment of the spring of the armature. It is estimated that the lag in these pens was not more than 0 001 second. One pen recorded the transits of the meniscus, the seconds given by the pendulum clock, and the marks manually impressed by the key, IK, to identify the seconds of the clock. The other pen recorded the seconds and tenths of seconds given by another clock driven by a synchronous electric motor. This electric clock was made by the General Radio Company and is their type 511S. The rate of this clock depended on the frequency of alternations of the power supplied by the Cambridge Electric Light Company. The records of this clock were only used to subdivide the full seconds given by the pendulum clock. Unless the rate of this electric clock varied by more than 1% within the second in which the transit of the meniscus occurred, its records are reliable to within 0.01 second for the purpose of subdividing the full seconds. With this arrangement the velocity of the paper tape would have to vary by 10% within the 0.1 second in which the transit occurred to cause an error of 0.01 second. It seems probable that the timing mechanism was reliable to within 0.01 second.

After many months of apparently fruitless effort and disappointments following changes in the equipment, the eventful day arrived when seven successive runs with water gave results for the time of flow which differed by only 0.01 second between the highest and lowest of the seven, out of a total of 618 seconds. This demonstrated that the optical effect of the passage of the meniscus was sufficiently definite and that the timing mechanism and temperature control were adequate. But these observations were made on one filling of the viscometer. The problem of cleaning ahd refilling the viscometer without changing the period still gave us much trouble and indeed has not yet been completely solved. Absolute cleanliness is essential as a trace of grease or dust will give erratic results. Cleansing reagents can make as much trouble as the more obvious forms of dirt. Indeed on one occasion the period increased from one filling to the next by nearly a second and the new high value for the period persisted for about two months in spite of drastic cleaning and then suddenly and inexplicably returned to its old value. The most plausible hypothesis to account for such a large change is that a speck of dust had become lodged in the capillary although it was not revealed by careful inspection. We have found it essential that every thing which enters the viscometer (water, solutions, cleansing reagents, and the air used to dry the instrument) should be filtered through a sintered glass filter or a platinum sponge filter. The sintered glass filter was made for us of Pyrex glass by H. E. Bent.[12]

If the volume of the working liquid is varied the hydrostatic head will change and this will influence the period. Therefore we filled the viscometer by means of a special pipet with a goose-neck delivery tube designed to deliver as definite a volume as possible each time and yet permit the actual volume delivered in each experiment to be determined by weighing the pipet to milligrams before and after filling the viscometer. If the amount actually delivered differed by a significant amount from the standard volume (about 60 ml.) a correction to the measured time was applied, based on the results of special experiments showing that a surplus of 0.013 ml, caused the time of flow to be increased by 0.01 second. After skill in the manipulation of the pipet had been acquired by practice the volume correction averaged less than 0.01 second. The delivery tube was broken accidentally twice during the experiments and after being repaired delivered a slightly different standard volume which caused a corresponding difference in the water value. The water value was also changed by slight but significant amounts in the course of the work by adjustments in the optical system, by remounting the viscometer in its frame, and by a redetermination of the 25° mark on the Beckmann thermometer after it had been lost by overheating. All of these changes, however, affect the solutions to the same extent as the water. Since we could not be sure that the water value would remain unaltered it was our invariable practice to measure water and a solution alternately and always measure the water at least once on the same day that the solutions were measured. After the technique had been perfected successive measurements of the time of flow without refilling rarely differed by more than 0.02 second and different fillings made on different days usually agreed within 0.03 second although occasionally much greater variations occurred for the reasons explained above. The viscosity of the solutions is computed with a water value determined within four hours of the time of measuring the solution instead of an average (or standard value) and the results for the relative viscosity of the solutions thus obtained are more consistent than can be obtained by assuming the water value to be unchanged.

The kinetic energy correction was applied to the results in all cases in which it amounted to 0.001% or more, in accordance with a method suggested by Bingham.[13] The greatest correction which needed to be applied was only 0.00013 in the case of 0.02 molal sucrose solution.

The density of the solutions enters into the calculations of the relative viscosity as a direct factor and therefore needs to be known with the same precision as the time of flow. For this reason the density of all of the solutions was determined by the use of pycnometers of about 50 cc. capacity. The densities were determined with greater precision than the time of flow could be determined.

Materials.—The water used both for making up the solutions and to determine the period of the viscometer was conductivity water, collected in contact with the laboratory

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[12] W. E. Bruce and H. E. Bent, THIS JOURNAL, **53**, 990 (1931).

[13] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1922, p. 18.

air and kept in large Non-Sol bottles. Its conductivity was determined before it was used and if the conductivity was found to be abnormally high the water was rejected. The average conductivity was 1.0×10^{-6} at 25°. All of the materials used are believed to have contained no impurities in sufficient amounts to affect the results measurably. The most dangerous impurity would be specks of dust. The purest salts available by purchase were dissolved, filtered through sintered glass filters, crystallized, drained and washed in platinum Gooch crucibles in a centrifuge. This entire process was repeated several times for some salts, but not in all cases, depending on the purity of the salts as judged by the color in the flame or other tests. Potassium chloride was fused and the other salts subjected to prolonged drying in vacuum desiccators. The cesium nitrate was kindly prepared for us from the mineral pollucite by Professor Brainerd Mears of Williams College. Spectroscopic and chemical tests showed that this material was of the highest quality.

Two non-electrolytes, sucrose and urea, were studied in order to test the theoretical prediction that the viscosity-concentration curves for electrolytes and for non-electrolytes would have an essentially different shape at low concentrations. It was, therefore. especially important to ensure that these materials should be as free as possible from electrolytes. This was, of course, easily tested by measuring the conductivity of the solutions. The sample of sucrose was estimated by conductimetric analysis to contain about 0.001% of electrolytes which could not influence the viscosity measurably. Since dilute sucrose solutions are liable to change by inversion or fermentation, the solutions were measured as promptly as possible after they were prepared. A special experiment showed no measurable change in viscosity after standing for forty-eight hours.

Sterling's C. P. urea was treated twice by the procedure described above for salts. Solutions of urea may be slowly hydrolyzed to form ammonium carbonate, and this change was easily detected by a slow change in the conductivity.

The conductivity of our freshly prepared solution indicated that it had hydrolyzed to the extent of nearly 0.002%, which increased to nearly 0.02% after standing for twenty-four hours in the conductance cell (in contact with the platinum electrodes which may have catalyzed the reaction). The strongest urea solution measured was 0.2 molal and even assuming 0.02% hydrolysis, which is probably an overestimate since the viscosity measurements were made promptly after preparing the solution, the concentration of the ammonium carbonate would have been only 0.00004 molal and therefore could not have influenced the viscosity measurably.

The solutions were prepared by weighing out the solute and making up the solution to 1 liter in a volumetric flask at 25°.

The data on the solution of 0.1 *N* potassium chlorate are given in considerable detail in Table I in order to show the concordance of the data obtainable with our new procedure.

The first line gives the concentration, *c*, of the solution in moles per liter at 25° and the date of the experiment; the second line gives the density at 25°, based on 0.997074 for the density of water at the same temperature with the letters B, C, D designating the different pycnometers used and av. the average. The numbers 1, 2, 3, designate the successive measurements of the time of flow on the same filling of the viscometer. The viscometer was filled with solution giving the results shown in the second column, then washed and dried and filled with water giving the results shown in the third column and again filled with another portion of the same solution giving the results shown in the fourth column. The figures designated by wt. are the weights of water or solution delivered by the filling pipet. The next line gives the volume correction (v. c.) in seconds to correct for the influence on the measured time of the variations in average hydrostatic head. The next line gives the average time of transit, t, with the volume correction applied. The next line gives the apparent viscosity, d_ct_c/d_0t_0, before the kinetic energy correction has been applied, and the last line gives the corrected relative viscosity, η, after applying the kinetic energy correction.

TABLE I

DETAILED EXAMPLE OR DATA

Potassium chlorate $c = 0.100000$ 11/25/31

d **B** 1.004691 C 1.004689 **D** 1.004684 av. 1.004688

Liq.	**Soln.**	**Water**	**Soln.**
1	612.77	618.32	612.77
2	612.78	618.33	612.77
3	612.77	618.32	612.75
av.	612.77	618.32	612.76
wt.	61.090	60.635	61.094
v. C	0.00	0.00	0.00
t	612.77	618.32	612.76
d_ct_c/d_0t_0	0.99859	0.99858	
Kinetic energy corr.	−0.00008	−0.00008	
η	0.99851	0.99850	

The data on the other solutions are given in a more abbreviated form in Table II to save space in printing. The column headings have the following significance: c, concentration in gram moles per liter, d_c is the density based on water at 25° 0.997074; t_c is the average time of flow for the solution; t_0 is the average time of flow for water; d_ct_c/d_0t_0 is the apparent relative viscosity with no kinetic energy correction applied; K. E. corr. is the kinetic energy correction; η obs. is the measured viscosity relative to that of water at the same temperature; η comp. is the viscosity computed by the equations given below.

for $KClO_3$ $\eta = 1 + 0.0050\sqrt{c} - 0.0309c$

KCl $\eta = 1 + .0052\sqrt{c} - .0140c$

KNO_3 $\eta = 1 + .0050\sqrt{c} - .0531c$

$KBrO_3$ $\eta = 1 + .0058\sqrt{c} - .0008c$

$CsNO_3$ $\eta = 1 + .0043\sqrt{c} - .092c$

NH_4Cl $\eta = 1 + .00566\sqrt{c} - .01439c$

Sucrose $\eta = 1 + .8786c$

Urea $\eta = 1 + .03784c$

$\Delta\eta$ = η obs. − η comp. is the difference between the observed and computed viscosity.

Interpretation of the Results

In Figs. 4, 5 and 6 plots of the results are shown with relative viscosity as ordinate and concentration as abscissa. These curves and the data on

TABLE II

RELATIVE VISCOSITY OF SALT SOLUTIONS AT 25°

Potassium Chlorate

c	d_c	t_c	t_0	d_ct_c/d_0t_0	K. E. corr.	η obs.	η comp.	An obs. − comp.
0.002001	0.997230	618.21	618.20	1.00017	0.00000	1.00017	1.00016	+0.00001
.005000	,997448	618.11	618.21	1.00021	.00000	1.00021	1.00020	+ .00001
.010000	,997830	617.86	618.22	1.00018	− .00001	1.00017	1.00019	− .00002
.020001	.998596	617.39	618.26	1.00012	− .00001	1.00011	1.00009	+ .00002
.050000	1.000892	615.68	618.28	0.99961	− .00004	0.99957	0.99957	− .00000
.100000	1.004688	612.76	618.32	,99858	− ,00008	,99850	,99849	+ .00001
Potassium Chloride at 25°								
0.002004	0.997160	618.20	618.14	1.00019	0.00000	1.00019	1.00021	−0.00002
.005011	.997312	618.27	618.23	1.00030	.00000	1.00030	1.00030	+ .00000
.010020	.997550	618.08	619.11	1.00040	.00000	1.00040	1.00038	+ .00002
.020041	.998023	618.71	619.02	1.00045	− .00001	1.00044	1.00046	− .00002
.035072	.998730	618.24	618.96	1.00050	− .00001	1.00049	1.00048	+ .00001
.050103	.999443	617.79	618.99	1.00043	− .00002	1.00045	1.00046	− .00001
		616.88	618.03	1.00051	− .00002			
.075154	1.000625	616.15	618.08	1.00042	− .00003	1.00039	1.00037	+ .00002
.100205	1.001790	615.35	618.08	1.00029	− .00004	1.00025	1.00024	+ .00001
.150309	1.004128	613.71	618.05	1.00000	− .00006	0.99994	0.99991	+ .00003
.200411	1.006463	612.14	618.15	0.99960	− .00009	,99951	,99952	− .00001
Potassium Nitrate at 25°								
0.001000	0.997134	618.86	618.82	1.00012	−0.00000	1.00012	1.00010	+0.00002
.002000	.997200	618.82	618.82	1.00013	− .00000	1.00013	1.00012	+ .00001
.005000	.997390	618.67	618.79	1.00012	− .00000	1.00012	1.00009	+ .00003
.010004	.997709	618.39	618.81	0.99996	− .00001	0.99995	0.99997	− .00002
.020000	.998336	617.82	618.81	.99966	− .00002	.99964	.99964	− .00000
.050001	1.000192	615.92	618.78	,99849	− .00004	.99845	.99846	− .00001
.100000	1.003283	612.77	618.83	.99637	− .00009	.99628	.99627	+ .00001
Potassium Bromate at 25°								
0.002001	0.997315	618.80	618.79	1.00026	0,00000	1.00026	1.00026	+0.00000
.005000	.997698	618.70	618.81	1.00045	.00000	1.00045	1.00040	+ .00005
.010000	.998294	618.38	618.77	1.00059	− ,00000	1.00059	1.00057	+ .00002
.020000	.999519	617.72	618.75	1.00078	− .00001	1.00077	1.00080	− .00003
.052994	1.003556	615.59	618.79	1.00130	− .00005	1.00125	1.00129	− .00004
.099999	1.009284	612.40	618.75	1.00186	− .00009	1.00176	1.00175	+ .00001
Cesium Nitrate at 25°								
0.000500	0.997140	618.19	618.20	1.000050	0.00000	1.00003	1.00005	−0.00002
.000500		618.83	618.86	1.000002	.00000			
.001000	.997205	618.20	618.28	1.000016	00000	1.00003	1.00004	− .00001
.001000		618.82	618.88	1.000034				
.002000	.997350	618.07	618.24	1.000002	.00000	1.00000	1.00001	− .00001
		618.73	618.90	1.000002				
.005000	.997788	617.72	618.25	0.999858	− .00001	0.99986	0.99984	+ .00002
		618.28	618.80	0.999875				
.010000	,998517	617.66	618.84	0.999537	− .00002	.99952	,99951	+ .00001
.020000	.999953	616.43	618.93	0.998836	− .00004	,99876	,99877	− .00001
		616.29	618.83	0.998771				
Ammonium Chloride at 25°								
0.002000	0.997115	618.89	618.79	1.00020	0.00000	1.00020	1.00022	−0.00002
.005000	.997162	618.74	618.60	1.00031	.00000	1.00031	1.00033	− .00002
.009999	.997248	618.91	618.74	1.00045	.00000	1.00045	1.00042	+ .00003
.020000	.997423	618.81	618.71	1.00051	.00000	1.00051	1.00051	+ .00000
.050000	.997940	618.50	618.70	1.00054	− .00000	1.00054	1.00055	− .00001
.100005	.998789	617.87	618.70	1.00037	− .00001	1.00036	1.00035	+ .00001
.200000	1.000473	616.44	618.74	0.99968	− .00003	0.99965	0.99965	− .00000

TABLE III

RELATIVE VISCOSITY OR SOLUTIONS OF NON-ELECTROLYTES AT 25°

Sucrose

c	d_c	t_c	t_0	d_ct_c/d_0t_0	K E. corr.	η obs.	η comp.	An obs. − comp.
0.000200	0.997094	618.34	618.23$_5$	1.00019	+0.00000	1.00009	1.00018	+0.00001
.000500	.997137	618.45	618.22	1.00043	+ .00001	1.00044	1.00044	+ .00000
.001000	.997194	618.75	618.27	1.00090	+ .00001	1.00091	1.00088	+ .00003
.002000	.997332	619.15	618.25	1.00172	+ .00001	1.00173	1.00176	− ,00003
.005000	.997714	620.50	618.21	1.00435	+ .00003	1.00438	1.00439	− .00001
.010000	.998391	622.83	618.29	1.00867	+ .00007	1.00874	1.00879	− .00005
.020001	.999699	627.36	618.21	1.01747	+ .00013	1.01760	1.01757	+ .00003

Urea

c	d_c	t_c	t_0	d_ct_c/d_0t_0	K E. corr.	η obs.	η comp.	An obs. − comp.
0.002000	0.997106	618.32	618.30	1.00006	+0.00000	1.00006	1.00008	−0.00002
.005000	,997152	618.35	618.28	1.00019	.00000	1.00019	1.00019	+ .00000
.010001	.997230	618.42	618.30	1.00035	.00000	1.00035	1.00038	− .00003
.020000	,997390	618.54	618.27	1.00076	.00000	1.00076	1.00076	+ .00000
.050033	.997867	618.97	618.32	1.00185	+ .00001	1.00186	1.00189	− .00003
.099994	.998666	619.61	618.30	1.00372	+ .00002	1.00374	1.00378	− .00004
.199632	1.000252	620.98	618.29	1.00755	+ .00004	1.00759	1.00755	+ .00004

which they are based show that the prediction of Jones and Dole that even those salts which decrease the viscosity of water at moderate concentration will give an increased viscosity at sufficiently low concentration has been confirmed experimentally at 25° for five salts, potassium chlorate, potassium chloride, ammonium chloride, potassium nitrate and cesium nitrate.

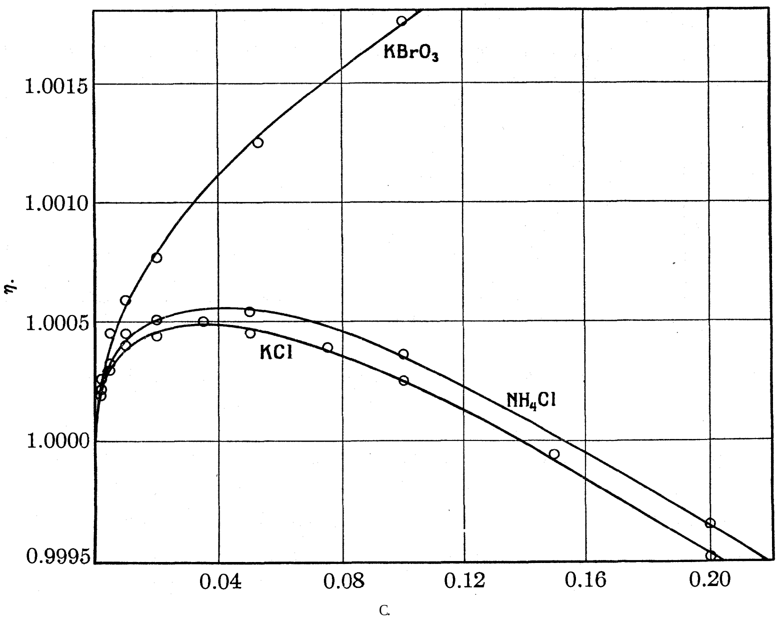

Fig. 4.—Relative viscosity-concentration curve for potassium bromide, ammonium chloride and potassium chloride.

In addition, the prediction has been confirmed by Joy and Wolfenden for potassium chloride, potassium chlorate, and rubidium nitrate at 18° and for rubidium nitrate at 35°. In the case of potassium bromate the viscosity remains greater than that of water throughout the range of concentration covered by our experiments (up to 0.1 molal).

Jones and Dole demonstrated that for barium chloride, which is presumably typical of the salts which increase the viscosity of water, the fluidity–concentration curves have a simpler form than the viscosity–concentration curves and that the equation $\varphi = 1 + A\sqrt{c} + Bc$ is valid up to 1 molal.

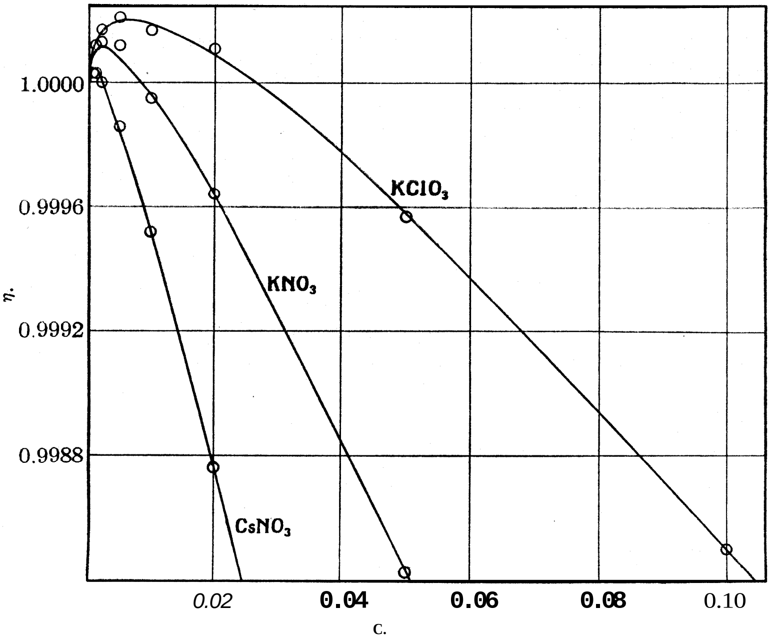

Fig. 5.—Relative viscosity–concentration curve for potassium chlorate, potassium nitrate and cesium nitrate.

In this equation A is expected to have a negative value for all salts and B may be either positive or negative, depending on the salt and temperature. On the other hand, for salts which diminish the viscosity of water this equation is probably not generally valid beyond 0.2 molal. For such salts it will probably be better to use an equation of similar form in terms of viscosity, namely, $\eta = 1 + A\sqrt{c} + Bc$, where the A is the same as the A in the fluidity equation except for a reversed sign, and the B will also be reversed in sign and identical in value within the limit of error to which B has yet been determined. The substantial equivalency of the two forms for dilute solutions ($c << 1$) will be apparent by replacing φ by $1/\eta$ and taking the reciprocal of both sides of the equation, making due allowance for the fact that *A* and B are much smaller than unity for all salts yet studied. When the equation is stated in terms of viscosity *A* is expected to be positive for all salts and zero for non-electrolytes. *B* may have either a positive or negative value depending on the salt and the temperature.

The equation $\eta = 1 + A\sqrt{c} \pm Bc$ may be readily transformed into $(\eta - 1)/\sqrt{c} = A \pm B\sqrt{c}$. This equation may therefore be most conveniently tested by plotting $(\eta - 1)/\sqrt{c}$ against $\sqrt{c}$ which should give a straight line whose intercept on the vertical axis is *A* and whose slope is ***B*****.**

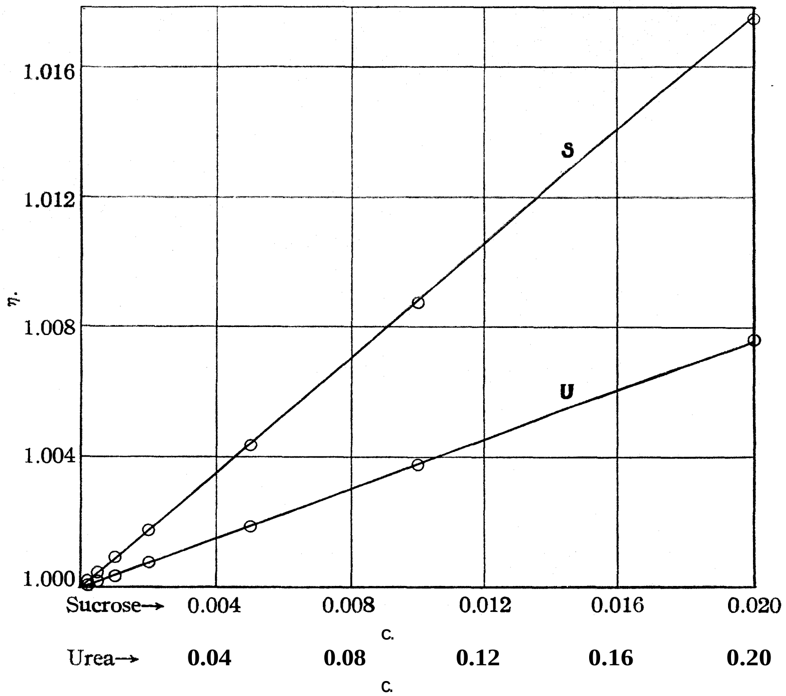

Fig. 6.—Relative viscosity-concentration curves for sucrose and urea.

As will be seen from Pigs. 7 and 8 the plotted data lie on a straight line and the value for *A* is positive for all the salts and zero for sucrose and urea. The values for *A* and *B* were selected by the use of the method of least squares instead of by plotting because the algebraic procedure is more precise and entirely objective. In the last column of Table III are given the differences between the observed viscosity and the viscosity computed by this equation with the values of coefficients *A* and *B* given in Table IV below. The average deviation, disregarding the sign, is 0.0015% which corresponds to an error in the time of flow of only 0.01 second. The maximum deviation for any of the forty-two solutions measured is 0.005% which corresponds to an error in the time of flow of 0.03 second.

This maximum deviation is probably accounted for by the fact that this particular measurement was made during a period of hot weather when the temperature of the room was above 25° which makes the control of the temperature less satisfactory than during cooler weather. The Jones and Dole equation is therefore confirmed for these six salts within the limit of error of the experiments.

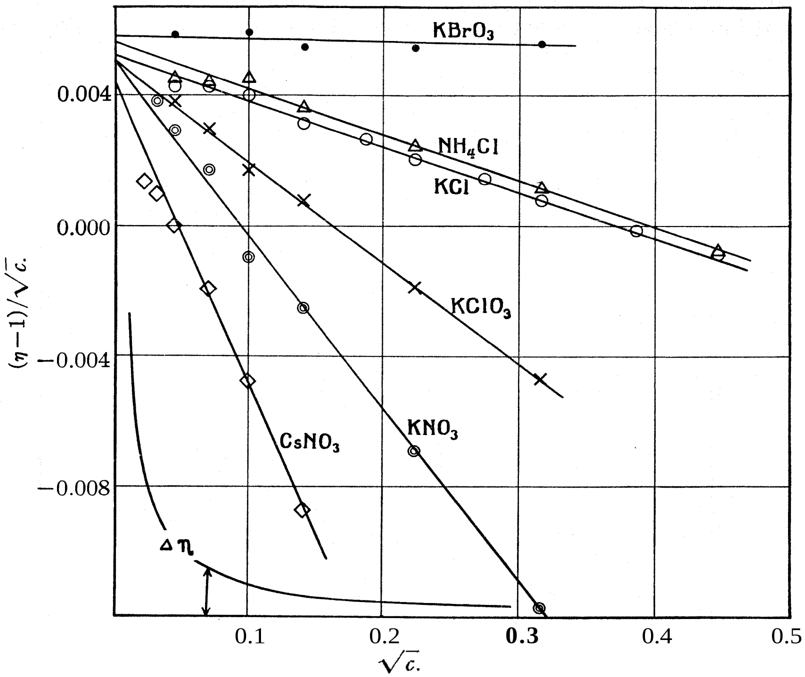

Fig. 7.—$(\eta-1)/\sqrt{c}$ against $\sqrt{c}$ for electrolytes: the curve $\Delta\eta$ shows graphically how a variation of 0.01% in η affects the data as plotted above.

The experimental values of A and B, computed by the method of least squares from the data above to fit the Jones and Dole equation, are shown in the following table and compared with the theoretical values of A computed by the Falkenhagen and Vernon equation. This equation reduces to the following form for the case of a uni-univalent salt

$$A = \frac{1.45}{\eta_0\sqrt{2D_0T}}\left[\frac{l_1 + l_2}{4l_1\,l_2} - \frac{(l_1 - l_2)^2}{(3+\sqrt{2})l_1\,l_2\,(l_1+l_2)}\right]$$

where η_0 and D_0 are the absolute viscosity and dielectric constant of water at the temperature T and l_1 and l_2 are the equivalent conductances of the two ions at zero concentration.

The coefficient of the linear term (B) varies much more from salt to salt and has a greater temperature coefficient than the coefficient of the square root term (A). For most salts the sign of B will be positive in the viscosity

TABLE IV

VALUES OF THE CONSTANTS IN THE EQUATION $\eta = 1 + A\sqrt{c} + Bc$

Solute	B J. & D. experimental	A J. & D. experimental	A F. & V. theoretical
KCl	−0.0140	0.0052	0.0050
$KClO_3$	− .0309	.0050	.0055
$KBrO_3$	− .0008	.0058	.0058
KNO_3	− .0531	.0050	.0052
NH_4Cl	− .01439	.0057	.0050
$CsNO_3$	− .092	.0043	.0051
Sucrose	+ .8786	0	0
Urea	+ .03784	0	0

equation (or negative in the fluidity equation). Little is known as yet in regard to the factors which influence the sign and value of this coefficient.

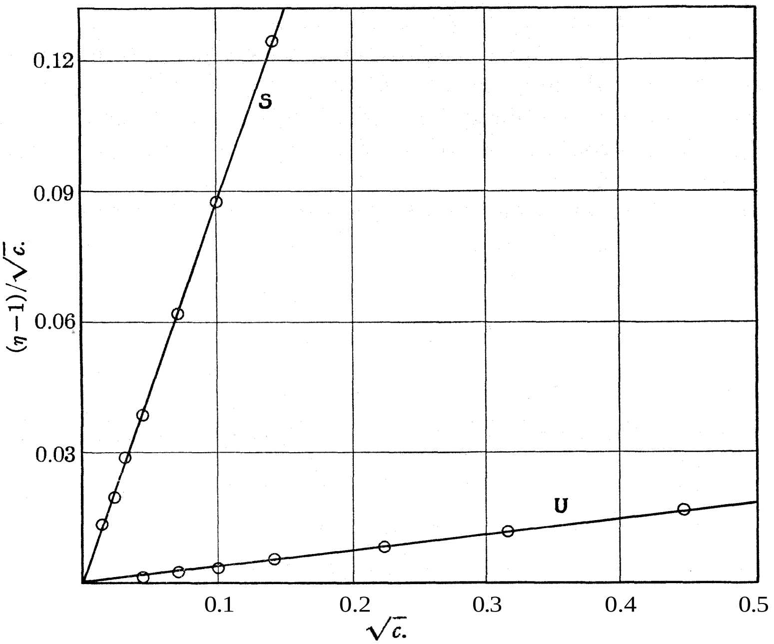

Fig. 8.—$(\eta-1)/\sqrt{c}$ against $\sqrt{c}$ for the non-electrolytes sucrose and urea.

The agreement between the observed and computed values is good and supports the Falkenhagen and Vernon equation for A. According to the Falkenhagen and Vernon equation the value of A for any given salt, solvent, and temperature will depend mainly on the valence type of the salt and to a less extent on the mobilities of the ions concerned. The results obtained up to the present time are in harmony with these conclusions as far as they go.

The results on extremely dilute solutions of sucrose and urea confirm the theoretical prediction that square root term will be absent for non-electrolytes.

It is planned to continue the work in this Laboratory by measurements on other salts, at other temperatures, and in other solvents.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

1. A new method for the automatic measurement of the time of flow of the liquid in a viscometer of the Ostwald type by means of a photoelectric cell is described. The elimination of the psychological errors inherent in the older technique permits greater precision.
2. The viscosities of dilute aqueous solutions of six salts and two non-electrolytes have been measured at 25°.
3. The results confirm the prediction made by Jones and Dole based on the Debye theory of interionic attraction that all salts will increase the viscosity of water if measured at sufficiently low concentration, including those salts which give a diminished viscosity at moderate concentrations.
4. The results confirm the Jones and Dole equation for the viscosity of solutions of electrolytes.
5. The results also confirm the Falkenhagen and Vernon equation for the computation of the influence of interionic attraction on the viscosity

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The Solubility of Nitrates in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND HARRIET A. GEER

Introduction

Although several investigations have recently been carried out upon various properties of solutions of salts in anhydrous acetic acid, quantitative solubility data for such solutions are still very meager. Aside from some early work on halides of mercury,(1) calcium and magnesium,(2) and antimony,(3) and the studies of acetates (bases in this solvent) reported from this Laboratory,(4) the only accurate solubility measurements have been those of Seward and Hamblet(5) on potassium perchlorate and potassium nitrate, at a single temperature, in the presence of varying amounts of added salts.

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(1) Étard, Ann. *chim. phys.*, [7] 2,555 (1894).

(2) Menschutkin, Z. *anorg. Chem.*, 54, 89 (1907).

(3) Menschutkin, J. *Russ Phys.-Chem. Soc.*, *43*, 1785 (1911); *Chem. Abstracts*, 6, 1280 (1912).

(4) (a) Davidson and McAllister, THIS JOURNAL, **52**, 507, 519 (1930); (b) Davidson and Griswold, *ibid.*, **53**, 1341 (1931).

(5) Seward and Hamblet, *ibid.*, 54, 554 (1932)

It was mentioned in a previous paper[6] that a large number of nitrates are appreciably soluble in acetic acid. In the present investigation, solubility data were determined over a wide range of temperature for the nitrates of silver, sodium and ammonium, and for barium nitrate at a single temperature. In the case of ammonium nitrate the determinations were continued to the melting point of the pure salt, so as to cover the entire range of concentrations; the freezing point curve thus obtained presents several interesting features.

Method

Preparation of Materials.—Pure anhydrous acetic acid was prepared as described previously.[7] The freezing point of the acid used in this work was from 16.55 to 16.60°. The salts were purified by recrystallization and thoroughly dried under suitable conditions; the purity of the silver nitrate and the ammonium nitrate was checked by analysis.

Determination of Solubility.—In the case of the silver, sodium and ammonium salts. the synthetic or freezing point method was used;[8] the determinations were carried out in large stoppered test-tubes provided with thermometer and stirrer as previously described. The thermometers were carefully calibrated before use. and each saturation temperature was determined at least twice. The measurements for sodium and silver nitrate were not continued beyond 100°, because of the inconveniently high vapor pressure of acetic acid at higher temperatures; ammonium nitrate, however, was so much more soluble at 100° that the vapor pressure was lowered sufficiently for the determinations to be continued up to the melting point, without change of method.

The accuracy of the determinations varies considerably with the rate of change of solubility with temperature. For the sodium and ammonium nitrate solutions, the equilibrium temperatures reported are believed to be correct to within 0.5°, a considerable portion of the ammonium nitrate data being more accurate than this. In the case of silver nitrate, a very faint turbidity, which persisted up to the boiling point, and may have been brought about by a slight solvolysis, was observed in all the solutions. Because of this fact, together with the extreme steepness of the freezing point curve, the equilibrium temperatures are less accurate; they are believed to be correct to within 1°.

The solubility of the barium nitrate proved to be so small that it could not be determined by the synthetic method. Instead, the concentration of solute in a solution saturated at a fixed temperature was determined by analysis. An excess of the salt was heated with 100 cc. of acid to 100° for forty-five minutes in a stoppered flask. The mixture was then cooled to room temperature, placed in a thermostat and allowed to remain at 30° for two days, with frequent stirring. The concentration of the solution was then determined by precipitation of the barium as sulfate. Because of the extremely small solubility, no high degree of accuracy is claimed for the result; it is correct to within 10%.

Analysis of Solid Phases.—Samples of the solid phases present at equilibrium were obtained by filtration, followed by rapid drying between porous tiles. The products so obtained were then analyzed to determine whether or not acetic acid of solvation was present. In the case of the silver nitrate solution, the solid was analyzed both for its silver content, by precipitation as chloride, and for acidity, by titration with sodium hydroxide solution; a rough colorimetric determination of nitrate, by means of phenoldisulfonic acid, was made also. The sodium nitrate was tested merely by titration

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(6) Davidson, THIS JOURNAL, 60, 1890 (1928).

(7) Ref. 4a, p. 508.

(8) A detailed discussion of the factors affecting the accuracy of this method has been given in a recent article by Sunier, *J. Phys. Chem.*, 34, 2582 (1930).

for acidity. In the case of the ammonium nitrate, the ammonia was determined by addition of excess of sodium hydroxide solution, followed by distillation into standard hydrochloric acid.

Results

The data obtained are tabulated below, and are represented also in the accompanying diagrams. Concentrations are expressed throughout in mole percentage of solute; T denotes the equilibrium temperature in °C.

I. Silver Nitrate–Acetic Acid

Solid phase silver nitrate

$AgNO_3$, %	0.0274	0.0398	0.0439	0.0708
T	30	36	40	54
$AgNO_3$, %	0.1035	0.1332	0.1361	0.1940
T	64	78	81	93

The solubility curve is shown in Fig. 1. The solid phase showed no measurable acidity; analysis for silver gave 62.30% (calcd. for $AgNO_3$, 63.49%). It is evident that the compound is unsolvated silver nitrate.

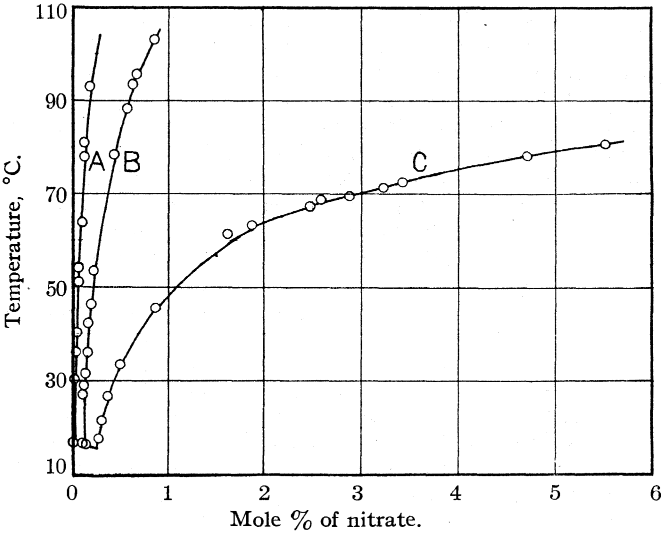

Fig. 1.—Solubility curves for $AgNO_3$ (A), $NaNO_3$ (B) and NH_4NO_3 (C) in anhydrous acetic acid.

A colorimetric test for nitrate gave results in accord with this conclusion. It has been reported[9] that when silver nitrate was treated with an excess of boiling acetic acid, colorless needles of a substance having the formula $(C_2H_3O_2)_2NOH(OAg)_2$ separated on cooling. This formula might equally well be written $Ag_2(C_2H_3O_2)NO_3.HC_2H_3O_2$, and the compound might be regarded as a solvated product of partial solvolysis (a basic salt of the acetic

[9] Pictet and Klein, Arch. *sci. phys. nat. Genève*, **15**, 589 (1903); J. Chem. *Soc.*, **84**, 1, 675 (1903).

acid system). No such compound could be isolated, however, in the present work.

II. SODIUM NITRATE–ACETIC ACID

(a) Solid phase acetic acid

$NaNO_3$, %	0.0	0.031	0.139	0.150
T	16.60	16.53	16.48	16.45

(b) Solid phase sodium nitrate

$NaNO_3$, %	0.122	0.139	0.150	0.166	0.173	0.183	
T	27.0	29.0	31.5	36.0	40.0	42.5	
$NaNO_3$, %	0.202	00.46	0.448	0.573	0.641	0.677	0.854
T	46.5	53.7	78.5	88.3	93.4	95.7	103.0

The solubility curve is shown in Fig. 1. The solid phase (b) showed no appreciable acidity, and is therefore unsolvated sodium nitrate.

III. AMMONIUM NITRATE–ACETIC ACID

(a) Solid phase acetic acid

NH_4NO_3, %	0.0	0.0741	0.1287
T	16.60	16.57	16.47

(b) Solid phase ammonium nitrate

NH_4NO_3, %	0.2832	0.3249	0.3916	0.5143	0.8745	1.634
T	17.7	21.4	27.0	33.6	45.8	61.2
NH_4NO_3, %	1.887	2.468	2.636	3.239	3.447	4.710
T	63.5	67.6	69.0	71.4	72.8	78.3
NH_4NO_3, %	5.508	7.255	8.620	13.68	17.15	19.36
T	80.9	85.7	89.0	97.1	101.0	102.6
NH_4NO_3, %	23.30	27.64	31.25	37.98	43.31	47.56
T	106.3	108.9	110.6	113.1	115.8	117.0
NH_4NO_3, %	51.67	55.5	60.1	63.1	66.8	71.6
T	118.3	120.0	121.4	122.9	124.8	128.9
NH_4NO_3, %	75.0	78.6	82.3	86.3	89.6	100.0
T	131.4	136.9	143.1	149.7	157.8	167.5

A small portion of the solubility curve is shown in Fig. 1, and the entire curve, on a smaller scale, in Fig. 2. Analysis of the solid phase (b) in equilibrium with solution at about 30° showed 20.00% of ammonia (calcd. for NH_4NO_3, 21.27%); since the upper portion of the curve terminates at the melting point of ammonium nitrate, the solid phase is evidently unsolvated salt throughout the entire range of concentrations.

Since ammonium nitrate is known to exist in four different crystalline modifications, at ordinary pressure, between −18° and its melting point,[10] the solubility curve might have been expected to exhibit sudden changes in slope at the transition temperatures, namely, 32.3, 84.2 and 125.2°; such discontinuities have, in fact, been observed in the solubility curve for this

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[10] The most recent discussion of the polymorphism of ammonium nitrate is given by Hendricks, Posnjak and Kracek, THIS JOURNAL, **54**, 2766 (1932).

salt in water.[11] In the acetic acid curve, however, these discontinuous changes must be much less marked, those at the two lower temperatures not being detectable at all in Fig. 2. A slight "break," however, may be observed at a temperature of 125°, corresponding to the change from the tetragonal (II) to the cubic (I) modification; this change, incidentally, is accompanied by a far greater heat of inversion than any of the others.

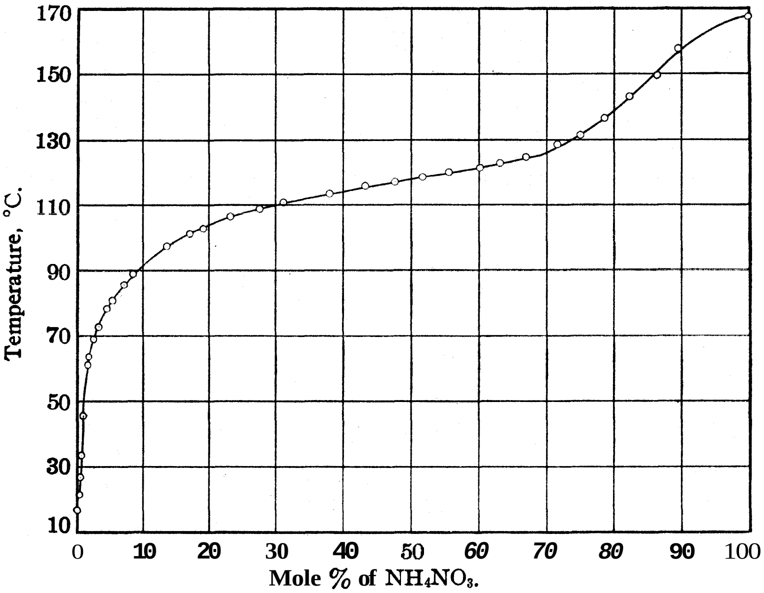

Fig. 2.—System NH_4NO_3–$HC_2H_3O_2$.

The form of the ammonium nitrate–acetic acid curve will be further discussed below.

IV. BARIUM NITRATE–ACETIC ACID

Solid phase $Ba(NO_3)_2$; solubility at 30°, 0.0005%

It was previously reported[12] that this salt was very slightly soluble and could be obtained as a precipitate upon mixing acetic acid solutions of barium iodide and sodium nitrate.

Discussion

The solubilities at 25° of the four salts here studied, together with that of potassium nitrate,[13] are shown in Table I; their solubilities in water[14] are included for purposes of comparison. In both solvents the solid phase is in every case the unsolvated salt.

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(11) "International Critical Tables," Vol. IV, p. 217.

(12) Ref. 6, p. 1893.

(13) Seward and Hamblet, Ref. 5, p. 568. (In the heading of the second column of Table II "$KClO_4$" appears, evidently as a typographical error, instead of "KNO_3").

(14) Ref. 11, pp. 217–240.

TABLE I

SOLUBILITY OF UNSOLVATED NITRATES IN ACETIC ACID AND IN WATER AT 25°

Salt	Solubility in acetic acid Mole, %	Solubility in acetic acid Moles per 1000 g. solvent	Solubility in water Moles per 1000 g. solvent
$Ba(NO_3)_2$	0.0005	0.00008	0.400
KNO_3	.105	.0175	3.74
$NaNO_3$	.121	.0202	10.80
$AgNO_3$	.020	.0033	14.00
NH_4NO_3	.370	.0619	26.98

The fact that interionic forces are much greater in acetic acid than in water makes the former a poorer "salt solvent."[15] Except for silver nitrate, solubility in acetic acid, in this series of salts, increases in the same order as in water; which, incidentally, corresponds to the order of decreasing melting points.

The discontinuous change in slope of the freezing point curve for ammonium nitrate at 125° has been mentioned above. Even aside from this "break," however, the entire course of the curve—steep in its initial portion, flattening out to a long central section of small slope, and becoming steeper again at a high concentration of salt—is of a decidedly unusual character. It resembles somewhat the curve observed for salicylic acid in water by Alexejew,[16] and that for silver perchlorate in benzene discussed by Hill,[17] each of which shows a point of inflection; but in the ammonium nitrate curve there are two distinct points of inflection, at 60% and at 85% of solute, respectively.

It is often of interest, in the study of solubility data, to plot them in the manner suggested by Hildebrand,[18] using as coördinates log N (where N is the mole fraction of solute) and $1/T$, the reciprocal of the absolute temperature at which solution and solute are in equilibrium. In the ideal case (for a solution obeying Raoult's law at all temperatures and pressures) this method of plotting yields a straight line whose slope is $-L_f/4.58$, where L_f is the molal heat of fusion of the solute.[19] In the case under consideration, since both components are polar to different degrees, and since they doubtless also differ considerably in internal pressure, wide and as yet unpredictable deviations from ideal behavior might be anticipated.[20] Nevertheless, it appeared to be worth while to plot the data, at least for that portion of the curve in the vicinity of the melting point of the solute, in the manner just described.

The molecular state of acetic acid in solution is not definitely known.

(15) Cf. Hammett and Dietz, THIS JOURNAL, 52, 4807 (1930).

(16) Alexejew, *Wied.* Ann., 28, 330 (1886).

(17) Hill, THIS JOURNAL, 44, 1163 (1922).

(18) Hildebrand, "Solubility," Chemical Catalog Co., Inc. New York, 1924, p. 148.

(19) If the heat of fusion varies with the temperature, there is a corresponding deviation from a linear relationship.

(20) Ref. 18, chapters VIII and IX. This system would not fall in the class of "regular" solutions, discussed at length by Hildebrand, THIS JOURNAL, 61, 66 (1929).

This compound is undoubtedly associated in the liquid state, both alone and in solution in many solvents,[21] and association is considerable in the vapor state also,[22] persisting even to temperatures well above the boiling point.[23] On this account, several writers,[24] in discussing systems containing acetic acid as one component, have considered it as having the formula $(C_2H_4O_2)_2$. While it is probable, in the present instance, that a considerable fraction of the acetic acid is in this form in solutions containing a large proportion of the solvent, at low temperatures, it is doubtful that such association would persist in solutions dilute in acetic acid, or at high temperatures. However, mole fractions have been calculated on the basis both of single and of double molecules (molar weight 120) of acetic acid, for purposes of comparison, and the resulting curves have been plotted in Fig. **3.** Each of these curves, it will be noticed, shows a slight "break" at a point corresponding to the transition temperature, 125°.

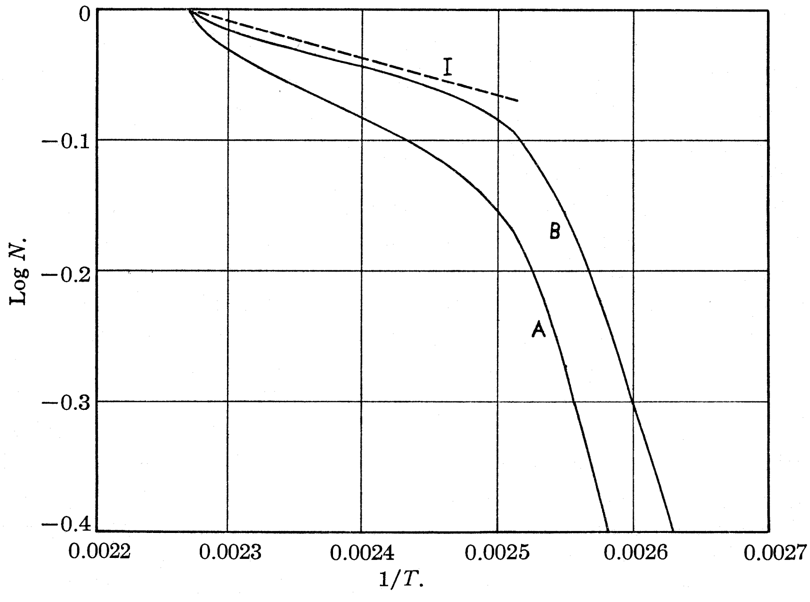

Fig. 3.—Solubility of ammonium nitrate in acetic acid: A, curve based on usual formula for acetic acid; B, curve based on formula $(C_2H_4O_2)_2$; I, approximate course of ideal curve.

The heat of fusion of ammonium nitrate has apparently never been determined by direct calorimetric measurement. However, Bridgman,[25]

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(21) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Inc., New York, 1931, pp. 173–174.

(22) Drucker and Ullmann, Z. *physik. Chem.*, *74,* 604 (1910).

(23) Trautz and Moschel, Z. *anorg. allgem. Chem.*, *155,* 13 (1926).

(24) Ward, *J. Phys. Chem.*, *30,* 1316 (1926); Roozeboom, "Heterogene Gleichgewichte," Brunswick, 1904, Vol. II, part 1, p. 260.

(25) Bridgman. *Proc. Am. Acad. Sci.*, **51,** 581 (1916).

in a study of the effect of pressure upon the polymorphism of this substance, calculated the heat of fusion, by means of the Clapeyron equation, from the rate of change of melting point with pressure, obtaining the value 6.9 kilogram-meters per gram, which is equivalent to the remarkably low value of 1300 calories per gram mole. Due to the difficulty in determining the increase in volume accompanying fusion, this value is probably not very accurate. In such an approximation, the unknown difference in heat capacity between the solid and liquid forms may be neglected, and the heat of fusion may be regarded as constant over a short temperature range.[26] Using the value of 1300 for L_f, we get -284 as the slope of the ideal curve between the melting point and 125°. This is represented in Fig. 3 by the broken line, the equation for which is $\log N = 0.644 - 284/T$.

It is evident that the experimental curve plotted on the basis of the usual formula for acetic acid deviates very widely from the ideal, even at low concentrations of acid, in the direction of smaller solubility. On the other hand, the curve plotted on the basis of double molecules of acetic acid approaches the ideal position rather closely at temperatures within 35° of the melting point; it is nearly linear over most of this range and has, in fact, practically the slope calculated from the approximate heat of fusion found by Bridgman. In the present state of our knowledge of this system, however, this approach to the ideal curve must be regarded as hardly more than fortuitous.[27] At lower temperatures the solubility appears to fall far below the ideal value; solvation presumably occurs only to a slight extent, if at all.

Summary

1. Quantitative solubility data have been obtained for ammonium, sodium and silver nitrates in acetic acid over a wide range of temperatures, and for barium nitrate at 30°. The solubility of these salts decreases in the order named. No solvates were isolated from any of the solutions.

2. A "break" occurs in the solubility curve of ammonium nitrate at 125°, due to the change in crystalline form which occurs at this temperature.

3. A plot of the logarithm of the mole fraction of ammonium nitrate against the reciprocal of the absolute temperature of equilibrium shows that the solution deviates widely from Raoult's law, as would be expected from the character of the components.

LAWRENCE. KANSAS

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(26) A further complication arises from the probable ionization of the ammonium nitrate, which, if complete, would result in a linear relationship between log $(2N/(N + 1))^2$, instead of log N, and $1/T$ (Ref. 18, p. 165). But the deviation produced by this factor is very small at high concentrations of solute—probably less, in this case, than the uncertainty of the heat of fusion—and has therefore been neglected in locating the ideal curve.

(27) Certainly we should not be justified in concluding that acetic acid was present entirely as double molecules under these conditions. The danger in drawing such conclusions as to the molecular state of substances in solution from the deviation of the solutions from Raoult's law has been repeatedly emphasized by Hildebrand (see, for instance, Ref. 18, pp. 83–84).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Solubility Studies. IV. The Solubilities of Certain Slightly Soluble Organic Compounds in Water[1]

BY PAUL M. GROSS, JOHN H. SAYLOR AND MARY A. GORMAN

In continuing a general program of research on the solubility in water and aqueous salt solutions of organic compounds in relation to their polar character,[2] the solubilities of an additional number of slightly soluble organic compounds in water have been measured. Since solubilities for most of these compounds are not in the literature, the value for the solubilities we have found are published now. The theoretical significance of these and other experimental values will be considered in a later paper.

Method.—The saturated solutions of the substances were prepared in thin-walled cylindrical flasks in a large water thermostat. The thermostat was kept at 30 ± 0.02°. The saturated solutions were analyzed by means of a Zeiss combination liquid and gas interferometer. The procedure has been previously described in detail.[2a]

Materials

Purification of Materials.—All of the organic chemicals were Eastman Kodak Company best grade with the exception of the cinnamic acid, which was a sample prepared in this Laboratory by Mr. William Miller, Jr. Solids were further purified by repeated recrystallization from an appropriate solvent until the melting points from two successive recrystallizations were the same. Liquids were purified by fractional distillation using for fractionations at atmospheric pressure a 25-cm. all-glass Widmer still and a small all-glass still with a 105-cm. column of the type previously described.3 A Hickman still, designed for a moderate vacuum with a barostat operated by a vacuum tube relay was used for distillations under reduced pressure. The thermometers used were a set of small two-tenth degree thermometers with a fifty degree range, calibrated by the Bureau of Standards; a set of fiftieth degree Goetze thermometers with a twelve degree range, calibrated by the Physikalische Technische Reichsanstalt; and for 1,3-dibromopropane, an uncalibrated tenth degree thermometer of good quality. Melting points down to −10° were determined with a tenth degree thermometer calibrated by the Bureau of Standards. For lower temperatures a pentane-filled degree thermometer with a range of 0 to −200°, calibrated by the Physikalische Technische Reichsanstalt was used. For distillations at atmospheric pressure the boiling points were corrected to 760 mm. by means of Craft's rule, whenever the value of dT/dp could not be found in the literature. Distilled water of good quality from the laboratory supply was used for the solubility determinations.

Table I summarizes the boiling point and melting point data for the samples used for the solubility determinations. The pressures during the vacuum distillations were maintained by the barostat within ±0.5 mm. of the values listed in column three.

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(1) Based upon a thesis submitted by Mary A. Gorman in partial fulfilment of the requirements for the M.A. degree at Duke University.

(2) (a) Gross and Saylor, THIS JOURNAL, 53, 1744 (1931); (b) Gross, *ibid.*, 51, 2362 (1929); (c) Gross, *Z. physik. Chem.*, B6, 215–220 (1929).

(3) Gross and Wright, *J. Ind. Eng Chcm.*, 18, 701 (1921).

TABLE I

DATA AND CONSTANTS FOR THE COMPOUNDS AND SOLUBILITIES IN WATER AT 30°

Substances	B. p. range, °C.	Pressure. mm.	M. p., °C.	Previously observed B. p., °C.	Previously observed M. p., °C.	Ref.	Grams per 1000 g. of water	Moles per 1000 g. of water	Estimated error, %
Diethyl ketone	101 **64–101.82**			**101.7**		**6**	**46.9**	**0.545**	**1.0**
I-Chloro-2-bromo-ethane	**106.62–106** 71			**106.7**		**4b**	**6.88**	**.0479**	1.0
1,3-Dichloropropane	**120.5–120.6**					**5**	2.87	.0254	1.0
Ethyl adipate	129.0–129.4	13	**−22**	**127**	**−21**	**4d**	4.26	.0211	0.5
Fluorobenzene	**84.55–84.63**			**85.14**	**(86)**	**8, 6**	**1.54**	**.0160**	1.5
***o*-Nitroanisole**			**9.2**		**9.4**	**6**	**1.69**	**.0111**	0.5
***o*-Nitroaniline**			**71.45**		**71.5**	**6**	**1.47**	**.0106**	1.5
***m*-Nitroaniline**			**111.7**		**111.8**	**6**	**1.21**	**.00877**	**1.0**
1.3-Dibromopropane	**166.64–166.86**			**166.95**		**4a**	**1.68**	**.00830**	**0.5**
***o*-Nitrotoluene**		9.4			**9.55**	**4e**	**0.652**	**.00479**	**2.0**
Cinnamic acid			**133.1**	**133.0**		**6**	**.604**	**.00408**	**1.0**
p-Nitroanisole			**53.9**		**54**	**6**	**.589**	**.00385**	**1.0**
***m*-Nitrotoluene**	118.0	20	**15.44**	**118.5**	**(15.55)**	**9, 6**	**.498**	**.00364**	**3.0**
***p*-Nitrotoluene**			**51.4**		**51.3**	**6**	**.442**	**.00322**	**0.5**
s-Tetrabromethane	**124.6–125.0**	19	**−1.0**	**123.7**	**0.13**	**4c**	**.651**	**.00188**	**2.0**
Iodobenzene	79 6–79.8	20		**78.4**		**7**	**.34**	**.0017**	**4.0**

Results

The solubilities of all of the substances measured and the estimated percentage errors are also given in Table I. The error was estimated from the concordance of duplicate determinations.

We have included ethyl adipate in the list of compounds measured, as a paper by Sobotka and Kahn[10] has recently appeared describing a rapid and simple solubility method applicable to certain liquids in which the solubilities of ethyl adipate and similar compounds were given. Our value at 30° of 4.26 g. per 1000 g. of water is in good agreement with the value found by the above authors which is 4.23 g. per 1000 cc. of water at 20°. Our results confirm the accuracy of their method.

Values for the solubilities of four of the compounds we have measured are given in the literature as follows, the temperature in all cases being 25° instead of 30".

Cinnamic acid, 0.546 g. per 1000 g. of water,'' 1.3-dichloropropane, 2.73 g. per 1000 g. of **water,**[2b] ***o*-nitroaniline,** 1.212 g. per 1000 g. of water, m-nitroaniline, 0.910 **g.** per 1000 g. of **water.**[12]

Allowing for the difference in the temperature of 5° our results are in

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(4) (a) Timmermans, Bull Soc. chim. *Belg.*, 28, 392 (1919); (b) ibid., 26, 300 (1912); (c) ibid., 27, 334 (1914); (d) ibid.. 36, 507 (1927); (e) ibid , **31,** 389 (1922).

(5) A sample previously purified by one of us. See Gross, THIS JOURNAL, **61,** 2362 (1929).

(6) "International Critical Tables."

(7) Young, J. Chem *Soc.*, **55,** 490 (1889). Attempts to fractionate iodobenzene under reduced pressure in carbon dioxide at atmospheric pressure resulted in some decomposition. By using the **Hickman** still and pressure regulator under a carbon dioxide atmosphere this was eliminated.

(8) Rechenberg, "Einfache und fractionierte Destillation in Theorie und Praxis." Schimmel and Company, 1923, p. 239

(9) Neubeck, *Z. physik.* Chem., **1,** 649 (1887).

(10) Sobotka and Kahn, THIS JOURNAL, **53,** 2935 (1931).

(11) Meyer, *Z. Electrochem.*, **17**, 978 (1911).

(12) Collett and Johnson. J. Phys. Chem., SO, 70–82 (1926).

good agreement with those for cinnamic acid and 1,3-dichloropropane. The discrepancy in the case of the nitroanilines is, however, larger than would be expected.

Summary

The solubilities in water of sixteen slightly soluble organic substances have been determined by means of an analytical method employing an interferometer.

DURHAM, NORTH CAROLINA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Dissociation Constant of Acetic Acid from 0 to 60° Centigrade[1]

BY HERBERT S. HARNED AND RUSSELL W. EHLERS

In a recent communication,[2] we showed that it was possible to determine the dissociation constant of a weak acid with very high accuracy from electromotive force measurements of the cells

$$H_2 \mid HAc\ (m_1),\ NaAc\ (m_2),\ NaCl\ (m_3) \mid AgCl \mid Ag$$

Values of the dissociation constants were determined from 0 to 35° inclusive at 5° intervals. More recently, we have obtained data from which this important constant may be obtained from 0 to 60° at 5° intervals. This determination involves values of the normal potential of the silver–silver chloride electrode through this temperature range. The values of this quantity which we shall employ have been revised slightly by us between 0 and 35° and determined between 35 and 60°.[3]

The method of calculation of K is described fully in our earlier contribution and was adhered to in all its detail. The equation for the electromotive force, E, of the cell is

$$E - E_0 + \frac{RT}{F}\ln\frac{m_{\mathrm{HAc}}m_{\mathrm{Cl}}}{m_{\mathrm{Ac}}} = -\frac{RT}{F}\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}\gamma_{\mathrm{HAc}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}} - \frac{RT}{F}\ln K \qquad (1)$$

E_0 is the normal potential of the cell, K, the dissociation constant, and the "m's" and "γ's" are the molalities and activity coefficients of the species denoted by subscripts. m_{HAc} and m_{Ac} were evaluated as previously described. As before, we let the right side of the equation equal $-RT/F \ln K'$, and then plot this quantity against μ. At zero μ, K' equals K. The extrapolation is easily carried out accurately as indicated by Fig. 1 of the former investigation. The value of K at 35° was redetermined and the

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[1] This contribution contains material which constituted a part of a Thesis presented to the Graduate School by Russell W. Ehlers in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1932.

[2] Harned and Ehlers, THIS JOURNAL, 64, 1350 (1932).

[3] The considerations and new data which have led to the review of the normal elctrode potential, E_0, will be published in another contribution.

result agreed with the revised result of the earlier data. In Table I are given the electromotive forces of the cells. In the present instance m_1, m_2 and m_3 were all at the same concentration. In the second part of the table are the values of K' and of K determined by extrapolation. The values of E_0 employed are given at the bottom of the table.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $H_2 | HAc (m_1), NaAc (m_2), NaCl (m_3) | AgCl | Ag$

$m_1 = m_2 = m_3$	E_{35}	E_{40}	E_{45}	Eso	E_{55}	Em
0.006313	0.64143	0.64511	6.64887	0.65247	0.65623	0.65980
,012869	.62267	.62594	.62936			.63943
.021015	.60965	.61281	.61596	.61898	.62215	.62534
.047973	.58775	,59049	.59331	.59594	.59873	.60146
.07613	.57553	.57802	.58067	.58316	.58569	.58821
.10031	.56837	.57083	.57316	.57561	.57799	.58039
,008419	.63386	.63738	.64091	.64447	.64796	.65149
.010131	,62895	.63239		.63939	.64279	.64624
.011845	,62474	.62815	.63155	.63493	.63829	.64165
.014868	.61875	.62201	.62533	.62858	.63184	.63509

VALUES OF K' AND EXTRAPOLATED VALUES OF THE DISSOCIATION CONSTANT K

$\mu =$			$K' \times 10^5$			
$m_2 + m_3 + m_H$	$t = 35°$	40°	45°	50°	55"	60°
0.01266	1.728	1.700	1.664	1.633	1.585	1.543
.02577	1.714	1.693	1.659			1.536
.04206	1.712	1.684	1.654	1.628	1.587	1.534
.09598	1.709	1.686	1.654	1.630	1.585	1.543
.14229	1.706	1.686	1.653	1.625	1.582	1.542
.20066	1.696		1.650	1.617	1.580	1.537
,01687	1.722	1.696	1.666	1.631	1.590	1.544
.02030	1.720	1.694		1.625	1.586	1.536
.02372	1.723	1.694	1.664	1.631	1.590	1.544
.02977	1.723	1.694	1.663	1.631	1.590	1.545
E_0 (obs.)	0.21563	0.21200	0.20821	0.20437	0.20035	0.19620
K X 10^5	1.729	1.701	1.668	1.633	1.590	1.542

One further refinement has been carried out. By the method of least squares, we have computed E_0 as a function of the temperature.[3] Its value is given by the equation

$$E_0 = 0.22239 - 645.52 \times 10^{6} (t - 25) - 3.284 \times 10^{-6} (t - 25)^2 + 9.948 \times 10^{-9} (t - 25)^3 \quad (2)$$

If we employ the values computed by this equation which are given in column two of Table II, we obtain the values of K in the third column. These we regard as our final values. At 25° our result of 1.754×10^{-5} checks very closely that of 1.753×10^{-5} recently determined by MacInnes and Shedlovsky[4] from conductance measurements. We have no accurate values with which to compare our results at other temperatures. In Fig. 1 we have plotted K against the temperature. All points except that at 30°

(4) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

fall on the smooth curve to within ±2 in the third decimal place which corresponds to an error of ±0.03 of a millivolt. It is apparent that K increases, reaches a maximum at about 23° and then decreases with increasing temperature.

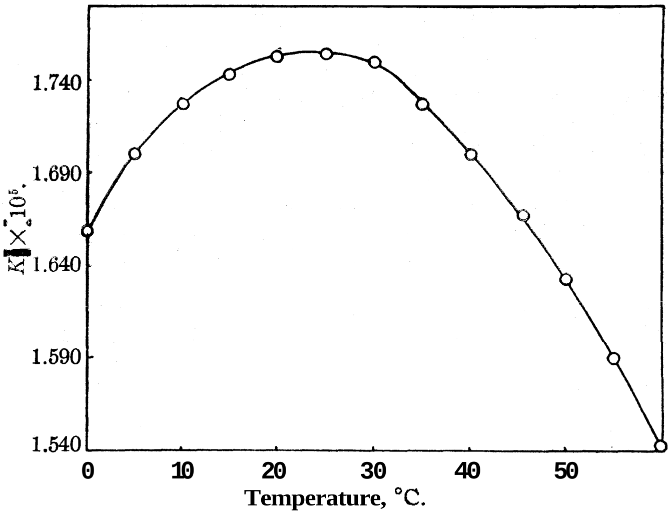

Fig. 1. —The dissociation constant of acetic acid as a function of the temperature.

To determine the heat content of ionization of the acid, we employed the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \text{or} \tag{3}$$

$$\frac{d \ln K}{d\,(1/T)} = -\Delta H \tag{4}$$

ln K was plotted against $1/T$, and A H was evaluated from the slope. A plot of these values of A H against T revealed that A H varied approximately linearly with the temperature. This suggested that the problem could be treated in the usual way. A H was taken to vary with the temperature according to

$$A\,H = a + bT + cT^2 \tag{5}$$

Upon substituting this value of ΔH in equation (3) and performing the integration

$$\log K = -\frac{a}{2.303\,RT} + \frac{b}{R}\log T + \frac{c}{2.303\,R}\,T + d \tag{6}$$

is obtained in which a, b, c and d are empirical constants. By substitution of the known values of K and T in equation (6), thirteen equations were obtained from which the constants were evaluated by the method of least squares. The equation with the empirical constants was

$$\log K = -\frac{1500.65}{T} - 6.50923 \log T - 0.0076792\,T + 18.67257 \tag{7}$$

Values of K computed by this equation are given in the fourth column of Table II. The differences between the observed and calculated results are given in the fifth column. At the higher and lower temperatures the calculated values are slightly higher than the observed, while in the middle range of temperature they are somewhat lower. We have previously noted this behavior when dealing with **a** similar calculation and function,[3] and found that another term, dT^3, is necessary in equation (5) in order to represent the results within the experimental error throughout the entire concentration raoge. In the present treatment, we have not resorted to this refinement. On the whole the agreement is good. The mean deviation is ±**0.003,** which corresponds to about ±**0.04** millivolt.

The equation for the change in heat content of the dissociation of acetic acid derived from equation (7) is

$$A\ H = 6871.0 - 12.94361' - 0.0351611'' \qquad (8)$$

Values of A H computed by this equation are given in the sixth column of Table II. In column seven, ΔC_p, the differences in specific heat of the ions and the undissociated molecule of acetic acid computed from the equation

$$\Delta C_p = -12.9436 - 0.070322T \qquad (9)$$

are compiled.

TABLE II

DISSOCIATION CONSTANT AND HEAT OR IONIZATION OF ACETIC ACID

t, °C.	E_0	K X 10^5 (obs.)	K X 10^5 (Equation 6)	A	AH	ΔC_p
0	0.23632	1.657	1.667	+0.010	714	−32.15
5	,23391	1.700	1.702	+ .002	552	−32.50
10	,23130	1.729	1.728	+ 002	389	−32.85
15	,22851	1.745	1.745	.000	223	−33.20
20	,22554	1.753	1.752	− .001	57	−33.55
25	,22239	1.754	1 751	− .003	− 112	−33.91
30	.21908	1.750	1741	− .009	− 282	−34.26
35	,21561	1.728	1.724	− .004	− 455	−34.61
40	,21200	1.703	1.700	− .003	− 628	−34.96
45	,20825	1.670	1.669	− .001	− 804	−35.31
50	,20436	1.633	1.633	.000	− 982	−35.66
55	.20033	1.589	1.592	+ .003	−1161	−36.02
60	.19620	1.542	1.547	+ 005	−1342	−36.37

Summary

1. Measurements of the cells

$$H_2 \mid HAc\ (m_1),\ NaAc\ (m_2),\ NaCl\ (ma) \mid AgCl \mid Ag$$

have been made from **35** to 60° at 5° intervals.

2. By a method previously described by us, the dissociation constant of acetic acid has been computed from **35** to 60° at 5° intervals from these results. Our earlier results from 0 to 35° have been recomputed by the use of more recently determined values of the normal potential of the silver–

silver chloride electrode. Final values of the dissociation constant of acetic acid from 0 to 60° at 5° intervals have been tabulated. Our value of **1.754** $\times 10^{-5}$ agrees excellently with the value, **1.753** $\times 10^{-5}$, determined from the conductance measurements by MacInnes and Shedlovsky.

3. The dissociation constant is given by the equation

$$\log K = -\frac{1500.65}{T} - 6.50923 \log T - 0.0076792T^2 + 18.67257$$

4. The heat of dissociation is given by the equation

$$AH = 6871.0 - 12.9436T - 0.035?61T^2$$

NEW HAVEN, CONNECTICUT
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Types of Chemical Reactions

BY WILLIAM ALBERT NOYES

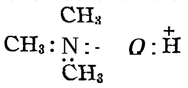
A study of the interaction of nitrogen trichloride with nitric oxide and with nitrogen tetroxide has given results from which, in conjunction with other experimental evidence and with current electronic theories, it is possible to define accurately, with a high degree of probability, the electronic course of several types of reactions.

The discussion which follows applies, primarily, to elements with atomic weights of 40 or below. For elements of higher atomic weights the outer shell of valence electrons seems to be less sharply defined.

Three principles are used. (1) On account of their "spin" and for other reasons, the electrons of the valence shell of an atom are usually, not always, associated in pairs, octets or sextets. (2) Every atom must have the positive charge of its nucleus balanced by the electrons immediately associated with it, or it must be an ion or form part of a complex ion, which is held to or in the neighborhood of another ion of the opposite sign, by static attraction. (3) In balancing the positive charge of the nucleus of an atom the pair of electrons of a covalence is equivalent to a single unshared electron.

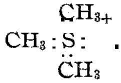
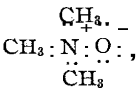
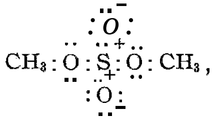
1. Formation of Ions

A. Permanent ions, formed with an outer shell of electrons (usually an octet) for some atom, in such a manner that the positive charge of the kernel or nucleus is overbalanced or underbalanced by the electrons surrounding it: (a) by the gain or loss of one or more electrons, as for sodium, calcium, chlorine or sulfur; (b) by the addition of a positive hydrogen or methyl ion to ammonia or to a tertiary amine, a positive hydroxyl group to a tertiary amine,



$\mathrm{CH_3:\overset{CH_3}{\underset{\ddot{C}H_3}{N}}:\cdot\ \mathit{O}:\overset{+}{H}}$

or a positive methyl to dimethyl

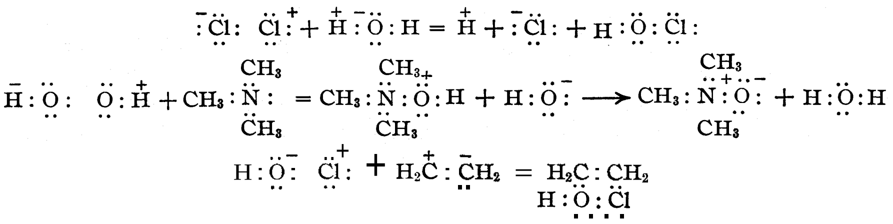
sulfide,  $CH_3:\overset{CH_3+}{\underset{CH_3}{\ddot{S}}}:$. In these cases the positive charge of the kernel of the nitrogen or sulfur atom is underbalanced because the sum of the covalence and unshared electrons is less than the number of their valence electrons. (c) By the removal of a positive ion from a covalence, as when the removal of a hydrogen ion from water gives an hydroxide ion, $H:\ddot{\underset{..}{O}}:^-$, in which the oxygen atom causes the ion to be negative because it has one covalence and six unshared electrons. The nitrogen and oxygen atoms of trimethylamine oxide,  $CH_3:\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}:\underset{..}{O}:^-$, and the two oxygen and the sulfur atom of dimethyl sulfate,  $CH_3:\ddot{\underset{..}{O}}:\overset{:\ddot{O}:^-}{\underset{:\underset{..}{O}:^-}{\overset{+}{\underset{+}{S}}}}:\ddot{\underset{..}{O}}:CH_3$, are held by one covalence and one ionic valence because the positive charges of the kernels of the nitrogen and sulfur atoms are underbalanced as they are in the ammonium and sulfonium ions, and because the positive charges of the kernels of the oxygen atoms are overbalanced as they are in the hydroxide ion.

Hydrogen ions are unique because they have no electrons. In general, hydrogen ions held by covalences ionize slightly, and since it is probable that hydrogen ions may be held by static attraction to atoms or molecules having complete octets it is often difficult to determine whether the atom is held in this manner or by a covalence. Physical methods are most suitable for an answer to this question.

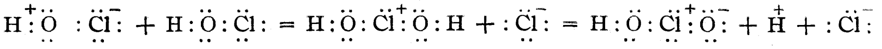
For these reasons reactions in which hydrogen ions are involved have an intermediate position between the ordinary ionic reactions and covalence reactions. The hydrogen ionization of water, of ammonia, of ethyl alcohol, of hypochlorous acid and of hydrogen atoms held by a covalence to carbon, is trifling, but it has been demonstrated by conductivity measurements in the first four cases. The ionization of hydrogen attached to carbon is important for an understanding of nitration and sulfonation reactions, the tautomerism of actoacetic ester and similar compounds, the Perkin, Kolbe and other condensation reactions involving the ionization of hydrogen atoms which are alpha to a carbon atom combined with oxygen, and many molecular rearrangements.

Some chemists have assumed negative hydrogen ions. It is doubtful if these ever occur in organic reactions.

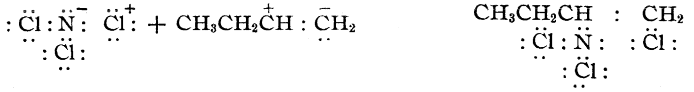
B. Six-electron-ephemeral ions are formed by the separation of two atoms held by a covalence in such a manner as to form a negative ion with a complete octet of electrons and a positive ion with only six electrons in the outer shell of the other atom. This is illustrated by the following equations



In this case both the hypochlorous acid and the ethylene form six-electron ions.



This is the first step in the formation of chloric acid from hypochlorous acid.



Because of the ephemeral character of positive, six-electron ions the evidence for their existence is indirect and similar to the evidence for organic radicals long used so successfully by organic chemists. In addition to the list given, they furnish a very simple explanation of nitration and sulfonation (the first step may be an addition), of the transfer and interchange of positive chlorine and hydrogen between nitrogen and carbon, of the interchange of methyl or phenyl groups and hydroxyl in other rearrangements, and of many intramolecular shifts of atomic attachments.

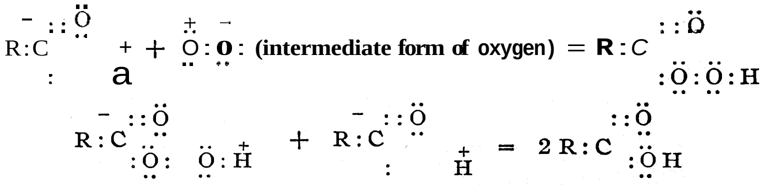
Because the evidence is indirect, we cannot expect complete agreement in the explanations given by different chemists. The situation is quite like that of tautomerism thirty to fifty years ago. We should be very careful to avoid dogmatism and should look diligently for experimental evidence for one view or another.

2. Ionic Reactions

A. Permanent Ions with Full Octets.—These are reversible and so rapid that the speed can rarely be measured. Three causes may make them nearly complete and may often reverse their direction: (a) formation of an insoluble or difficultly soluble product; (b) formation of a volatile product or of a compound which dissociates, giving a volatile product; (c) formation of a product which ionizes slightly, such as water, or which rearranges to a compound which ionizes slightly. Organic indicators belong to this class.

B. Covalence Reactions; Six-Electron Ions.—Such reactions are, superficially considered, very similar to the reactions of permanent ions, but there are important differences. One at least of the compounds reacting must be held together by a covalence; the number of six-electron ions is always very small and the speed of the reaction is frequently of such a rate that it can be measured; the covalence compounds formed may separate less readily than the original compounds and the reaction may be practically irreversible; covalence compounds may separate at different points and in different ways, causing different reactions to proceed at the same time—this is particularly true of organic compounds. Covalence compounds may also dissociate to electrically neutral parts with odd electrons and these free radicals (see below) may react in a different manner. Very often one of the reacting compounds and one of the products consist of permanent ions, as when methyl iodide reacts with silver nitrate. The same factors which cause reactions of permanent ions to become nearly complete are often important in covalent reactions.

The oxidation of aldehydes and ketones, recently discussed by Haber and Willstatter[1] and previously by Wieland, is probably of the covalence type

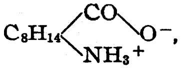


$$\underset{:\quad a}{\overset{-\,::\ddot{O}}{R:C}}\ {}^{+} + \overset{+\;\;-}{\ddot{O}:\ddot{O}:}\ \text{(intermediate form of oxygen)} = \underset{:\ddot{O}:\ddot{O}:H}{\overset{::\ddot{O}}{R:C}}$$

$$\underset{:\ddot{O}:}{\overset{-\,::\ddot{O}}{R:C}}\ \overset{+}{\ddot{O}:H} + \underset{:}{\overset{-\,::\ddot{O}}{R:C}}\ \overset{+}{H} = 2\,\underset{:\ddot{O}H}{\overset{::\ddot{O}}{R:C}}$$

In the last reaction positive hydroxyl and positive hydrogen exchange places. Wieland has shown that acid peroxides are formed in some of these reactions.

3. Dissociation and Reactions of Free Radicals

The term "electrolytic dissociation" was originally used for ionization. It helps to clearer thinking if we use the word dissociation to designate separations which give electrically neutral atoms or molecules, and ionization to designate all cases where the positive charge of the kernel or nucleus of some atom is not balanced by the electrons immediately associated with it. Such ions, or the groups which contain them, may separate from the ions of opposite sign in solutions, or may be held to them by static attraction while retaining their ionic character as sodium and chlorine are held together in crystals and probably in the gaseous state, as the ammonium and carboxyl ions are held together in aminolauronic acid, , and as atoms are held together in the semipolar unions of sulfuric acid and other compounds.

Dissociation is usually caused by heat, photochemical action or electrolysis. Typical examples are the dissociation of chlorine molecules to two chlorine atoms with seven electrons each; and the removal of an elec-

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(1) Haber and Willstätter, Ber., 64, 2849 (1931).

tron from the acetate ion in the electrolysis of sodium acetate. This is followed by the formation of a covalence between the oxygen atom which has lost the electron and the carbon of the carboxyl group, the other electron being taken from the covalence with the methyl. Carbon dioxide then separates in an electrically neutral state and the methyl, which is also electrically neutral, with its odd electron, immediately unites with another methyl radical to form ethane. Paneth and Rice have shown that similar free radicals may be formed by thermal dissociation and that such radicals are extremely reactive. Triphenylmethyl and similar compounds and the free radicals of nitrogen discovered by Wieland are more stable. Nitric oxide, an electrically neutral molecule with an odd electron takes an electrically neutral chlorine atom from nitrogen trichloride. The nitrogen dichloride unites with another mole of nitric oxide to form dichlorodinitrogen oxide. At −150° a third mole of nitric oxide takes an electrically neutral atom of chlorine from this compound.

Two atoms of sodium give their odd electrons to electrically neutral chlorine atoms, forming sodium chloride

$$2\mathrm{Na}. + :\ddot{\mathrm{Cl}}:\ddot{\mathrm{Cl}}: = 2\overset{+}{\mathrm{Na}} + 2:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\overset{-}{:}$$

In a similar manner two atoms of sodium give their electrons to a molecule of oxygen, forming sodium peroxide

$$\mathrm{Na}.\ \cdot\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\cdot\ .\mathrm{Na} \longrightarrow \mathrm{Na}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{Na}$$

The reaction of sulfite ions with cupric ions giving cuprous ions and dithionate ions, recently discussed by Haber and Willstätter,[2] is probably of this type

$$2(\mathrm{Cu}^{\underset{\cdot}{+}+}\cdot\mathrm{SO}_3^{=}) = 2\mathrm{Cu}^{+} + (\mathrm{O_3S{:}SO_3})^{=}$$

An electron is transferred from each sulfur atom to a cupric ion, reducing it to a cuprous ion. Then the sulfur atoms with odd electrons unite.

The decomposition of nitrogen trichloride and of acetylene and the chain reactions between hydrogen and chlorine and between hydrogen and oxygen, are almost certainly of this, class. When such reactions are strongly exothermic they will be explosive.

The catalytic hydrogenation reactions are very probably due to hydrogen atoms with odd electrons.

I wish to express my thanks to a number of my friends, who have kindly read this paper and whose criticisms have been very helpful.

Summary

Reactions are classified, in accordance with their electronic character, under three heads: (1) formation of ions; A, with complete octets; B, from covalences, one with eight electrons, one with six; (2) ionic reactions;

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(2) Haber and Willstatter. Ber.. 64, 2844 (1931).

A, ions with complete octets; B, ions formed from covalences; **(3)** dissociation and reactions of electrically neutral atoms and molecules.

The following principles, which the space allowed does not permit me to discuss, give a satisfactory explanation of the inorganic complexes: 4. Atoms may form covalence groups with a larger number of covalences than the number of valence electrons of the central atom. **5. A** valence electron may be transferred, either to form a negative ion which enters the complex or one that is exterior to the complex. **6. If** the "donor" (Sidgwick) is an electrically neutral molecule (ammonia or water), it becomes a positive ion in the complex; if it is a negative ion (Cl^-, NO_2^-), it becomes electrically neutral in the complex. **7.** The "acceptor," in every case, develops a negative charge for each covalence, which may be balanced by the positive charge of the "kernel" (Lewis), by the positive ions of the complex or by positive ions exterior to the complex.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

The Linear Thermal Expansion of a Single Crystal of Sodium Nitrate

BY J. B. AUSTIN AND R. H. H. PIERCE, JR.

The results of a recent series of studies of the physical properties of sodium nitrate conducted by Kracek[1] and his colleagues[2] have firmly established the existence of a gradual transition in the crystalline salt between 150 and 280°. The transition appears to be practically completed at 275° but abnormal changes in the heat capacity and volume are distributed over an extended temperature interval below this critical point.

The basis for a satisfactory explanation of the phenomenon seems to have been found in the theoretical treatment by Pauling[3] of the problem of the diatomic homopolar molecule free to rotate in an axially symmetrical field of force. His analysis together with the available x-ray evidence[2] makes it seem almost certain that during the transition interval the rotational degree of freedom of the nitrate ion about an axis normal to the plane of the group becomes excited. At the critical temperature this degree of freedom is fully excited and the nitrate ion begins to rotate about the trigonal axis of the crystal unit. The transition corresponds, therefore, to a change from oscillational to rotational motion for the nitrate ion.

One of the properties studied in detail by Kracek was the volume ex-

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(1) Kracek, THIS JOURNAL, **53**, 2609 (1931).

(2) Kracek, Posnjak and Hendricks, *ibid.*, **63**, 3339 (1931).

(3) Pauling, *Phys Rev.*, **36**, 430 (1930).

pansion of the salt. While his results serve admirably to demonstrate the existence of the transition they do not elucidate the very interesting question of the anisotropic expansion in various directions in the crystal. Such information is of considerable value in analyzing the nature of the changes which take place during the transition, and since a knowledge of the mechanism of these changes is of great importance in the theory of the solid state, we have undertaken a series of measurements of the expansion in several directions of known orientation in the crystal.

Material.—The sodium nitrate used in the experiments was recrystallized three times starting with the best material commercially available. It crystallizes easily so that single crystals of considerable size can be readily secured. A number of crystals were prepared and the clearest and most perfect ones were selected for use.

Apparatus.—The Pulfrich–Fizeau interference method as modified by the U. S. Bureau of Standards was employed in making the measurements. The principles of, and apparatus for, this method are described in the publications of the Bureau.[4] The only departure from the equipment therein specified was in the design of the furnace which is shown in Fig. 1. A porcelain tube, F, wound with a helical nichrome coil, K, is mounted vertically in a sheet iron jacket and is surrounded with Sil-O-Cel. A smaller tube, E, supports the porcelain cup, C, which contains the interferometer plates, S. A small bore porcelain tube holding the platinum–platinrhodium thermocouple passes through the bottom of the cup. C, the junction being so adjusted that it nearly touches the lower interferometer plate. The upper end of the furnace is closed by another porcelain tube containing the fused silica windows W_1 and W_2; W_3 is a glass window.

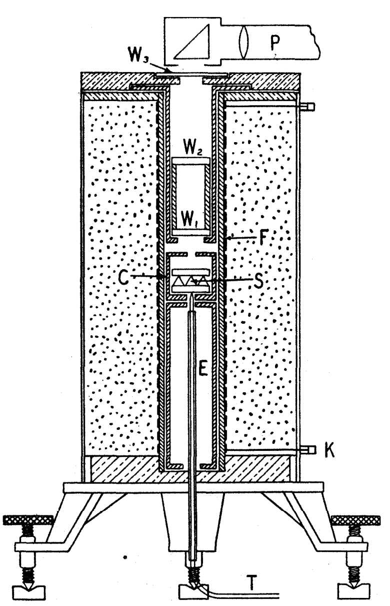

Fig. 1.—Apparatus for measuring linear thermal expansion.

The viewing apparatus is shown at P. The helium line at **5875.6 Å.** was used as a monochromatic source of illumination. With this light a change in length of $\pm 3 \times 10^{-6}$ cm. could be easily detected.

The thermocouple was checked in position in the furnace on the melting points of tin, aluminum and silver, and on the α-β inversion of quartz; it was also checked against a carefully calibrated refraction thermometer of fused silica. Temperatures were read on a Leeds and Northrup wall-type potentiometer which had been checked at the Bureau of Standards and are probably good to ±1° or better.

With this apparatus it is necessary to have three small specimens very nearly the same height. Preliminary experiments showed that the results obtained with a set of three small pyramids cut from one large crystal were more satisfactory than those obtained with specimens cut from three small crystals; hence for the final measurements a small slab was cut from a large crystal so that the normal to the surface of the slab co-

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[4] Peters and Cragoe, *Bur. Standards Sci. Papers* (No. 393), 16, 449 (1920); Peters and Boyd, *ibid.*, (No. 436), 11,677 (1922); Merritt, ibid., (No. 485) 19,357 (1924).

incided with the direction in the crystal along which the expansion was to be determined. Three small pyramids were then cut from this slab. Although this method of preparation does not orient the specimens with great accuracy it proved to be quite satisfactory for the present purpose.

Results

The expansion was measured in three different directions: parallel to the *a* axis, parallel to the *c* axis and perpendicular to the rhombohedral faces $(10\bar{1}1)$ and $(\bar{1}01\bar{1})$. For the first two directions two sets of specimens were examined; for the last direction but one was used.

The results obtained are given in Table I in the form of the increase in length per unit length and the true linear expansion coefficient; these values were taken from a smoothed curve drawn through the experimental points for all the determinations in a given direction. This procedure was rendered advisable by the fact that the curves for any single determination showed curious undulations, apparently connected with the efflorescence of the salt on heating, which were not reproducible and could be largely balanced out by combining the data for two runs. The curves themselves and the experimental points are shown in Fig. 2.

TABLE I

LINEAR EXPANSION OF SINGLE-CRYSTAL SODIUM NITRATE

I, °C.	Increase in length per unit length ($\Delta l/l_0$) in mm/m. (‖ a axis)	(⊥ $10\bar{1}1$ face)	‖ c axis	True linear expansion coeff. a 10^6 at t° (‖ a axis)	(⊥ $10\bar{1}1$ face)	(‖ *c* axis)
18	0.0	0.0	0.0	..	...	...
50	.35	2.5	2.8	11.0	74	120
75	.62	4.4	5.7	11.6	76	122
100	.93	6.3	8.9	12.0	78	132
125	1.22	8.3	12.3	11.4	80	138
150	1.50	10.3	15.8	11.0	82	142
175	1.77	12.4	19.4	10.6	84	152
200	2.03	14.5	23.4	10.5	106	184
225	2.30	17.7	28.6	10.4	148	234
250	2.55	22.4	35.1	10.0	210	368
260	2.65	24.7	38.6	10.0	235	445
270	2.75	27.3	44.0	10.0	320	600
295	2.80	29.0	47.0	10.0	540	660

The variation of the expansion coefficients with temperature is shown in Fig. 3a.

Aside from the slight irregularities mentioned the results were, with one exception, strictly reproducible, not only on heating and cooling but also from sample to sample. Such variations as do appear are well within the possible error arising from the uncertainty of the orientation and the measurement of the expansion.

The one exception is the contraction of the crystal above the critical temperature in the direction of the a axis, which was not reproducible even for the same sample on heating and cooling.

Unfortunately the set of specimens for the direction perpendicular to the $10\bar{1}1$ face suffered some irregular behavior in passing through the critical point at 275° and the fringes were lost, hence no measurements above this temperature are available for this direction.

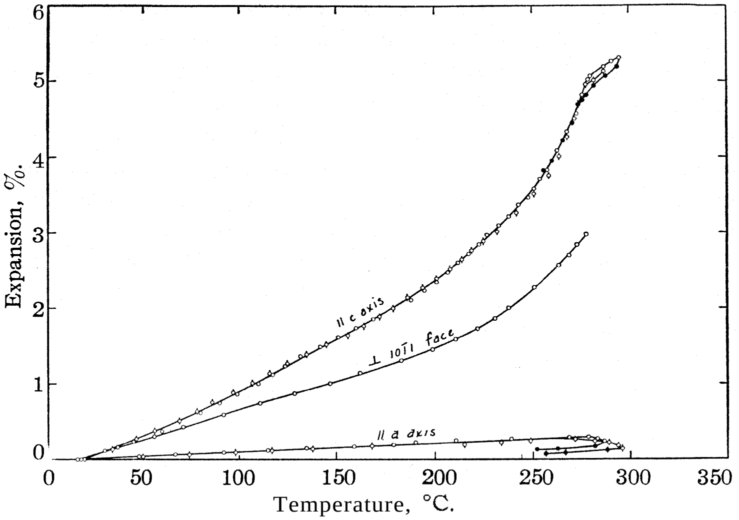

Fig. 2.—Linear expansion of single-crystal sodium nitrate in various directions in the crystal. O, first set of specimens; ϕ, second set of specimens; e, points obtained on cooling.

Discussion

The most striking feature of the data presented is the very large difference in expansion in the directions of the crystallographic axes. In the direction of the *a* axis the total expansion at 275° is only 0.3%, while perpendicular to this direction (parallel to *c* axis) it is 5% or 17 times as great. Anisotropy of this magnitude is extremely unusual, at least among the substances thus far described in the literature, and is to be accounted for by the abnormal increase in length along the *c* axis during the transition. It will be interesting to see whether, when other substances having the same type of transition are discovered, they will possess a similar behavior.

It is important to note that the effect of the transition along the *a* axis is extremely slight, if indeed it exists at all, since the expansion coefficient actually decreases slightly in the transition range. This fact together with the abnormal increase in length along the *c* axis leads to some important conclusions regarding the mechanism of the change.

In order to picture the relative motions of the various parts of the lattice it is necessary to have the structure of the lattice clearly defined. It appears to be well established that a number of nitrates, including sodium nitrate, owe their strong double refraction to the arrangement of the nitrate groups in parallel planes. It also appears that the metal ions lie in planes parallel to, and alternating with, the planes of the NO_3 group.

If the interpretation of the x-ray data by Kracek, Posnjak and Hendricks is correct the abnormal expansion between 150 and 280° is indicative of an increasing amplitude of oscillation of the NO_3 ions in the plane of the group and perpendicular to this plane, that is, the oscillation is about the trigonal axis of the crystal unit. It is also probable that actual rotation is present for a small number of ions during the transition interval, the proportion of such ions increasing with temperature.

Applying these concepts to the expansion data one is led to conclude that the increasing amplitude of oscillation results in a marked separation of the planes of the nitrate ions and metal ions without any abnormal increase in the dimensions in the plane of the group. In other words the intermolecular forces which are affected are those acting between the alternate layers of nitrate and metal ions whereas the forces acting in those planes remain substantially unchanged.

A more exact description can be made along the lines of Pauling's theoretical treatment. As the temperature is increased the energy level, *n*, of the nitrate ion will also change. When $n + 1$ becomes greater than a certain critical value, which depends upon the moment of inertia and the constant of the potential function (V_0), the motion becomes rotational. As n approaches the transition value the eigenfunctions change completely in nature, becoming more nearly constant This change increases the repulsive forces between alternate layers of nitrate ions and possibly between the layers of nitrate and metal ions resulting in a tendency to spread the crystal lattice as soon as an appreciable number of molecules have begun to rotate. But spreading the lattice decreases the forces between the layers and decreases V_0. This permits more molecules to rotate and the effect builds up to give increasingly greater expansion

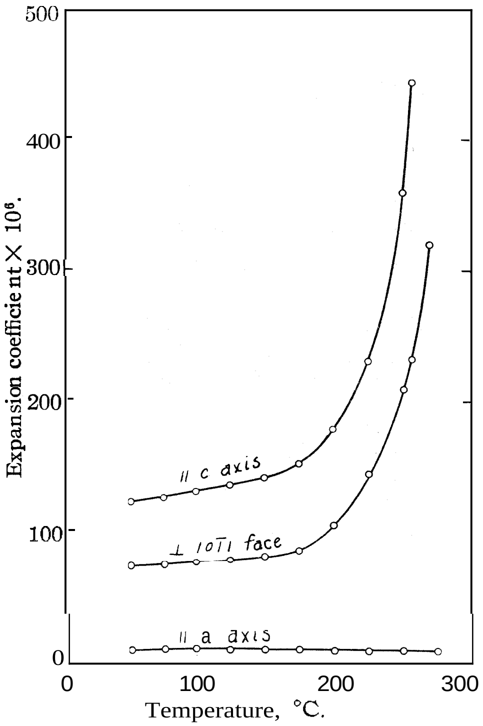

Fig. 3a.—True linear expansion coefficient of sodium nitrate in various directions in the crystals.

perpendicular to the planes of the NO_3 ions. When all the nitrate groups are rotating the effect is no longer observed.

So far rotation about an axis normal to the plane of the NO_3 group has been considered The ion has two other rotational degrees of freedom about axes in the plane of the group but these are apparently degenerate, as pointed out by Kracek, Posnjak and Hendricks, and hence will not be considered.

Attention should also be called to the irreversible contraction observed in the direction of the a axis when the critical point is passed. This effect may be due to an actual contraction of the specimen but it is also possible that in this region the crystal becomes so soft that it can no longer support the weight of the upper plate of the interferometer. While no definite choice can be made at present between these explanations, the fact that the contraction was not reproducible with different specimens renders the latter hypothesis slightly more acceptable.

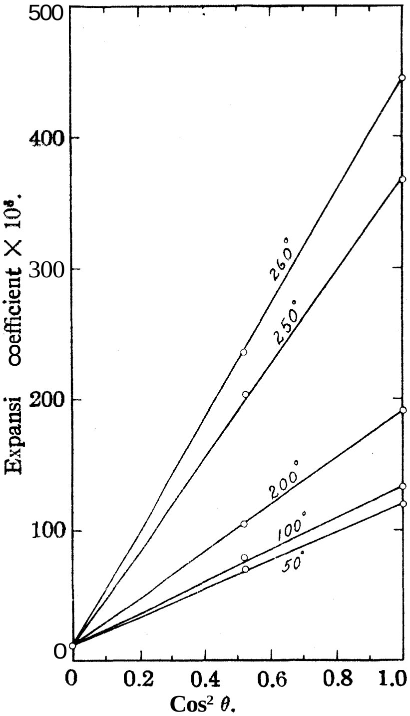

Fig. 3b.—True expansion coefficient a plotted as a function of cos² θ.

The abnormal increase in length along the c axis also leads to an appreciable decrease in α, that is, the angle between the axes of the true structural unit[5] as Kracek, Posnjak and Hendricks have already noted. Specifically they found that α decreased from 47°14' at 25° to 45°35' at 280°. If we assume for 25° the axial ratio a:c = 1:0.8297 which corresponds to $\alpha = 47°14'$, values of the axial ratio and of α for 280° can also be obtained from the expansion data. The axial ratio so computed is 0.8662, corresponding to an angle of 45°34', which is only one minute smaller than the angle calculated from the x-ray data. This agreement is most satisfactory.

As mentioned above the data for successive runs on the same set of samples and measurements on different sets gave results which showed that the effects observed were unquestionably reproducible. It can further be shown that the data for the three directions measured are consistent within themselves. The simplest manner of comparing the data for this purpose

(5) Cf. Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

is by means of the cosine-square law which states that in a crystal having hexagonal symmetry the expansion coefficient is a linear function of the square of the cosine of the angle between the direction of measurement and the principal axis of the crystal.

The expansion coefficients at a number of temperatures for the three directions studied are plotted against $\cos^2\theta$ in Fig. 3b. In plotting these curves no correction has been made for the change in the angle θ with temperature but for the set of measurements in the direction perpendicular to the rhombohedral faces it has been assumed to be 43°46′, the value at 25°, throughout. The neglect of this change is justified by the fact that it is quite small and introduces an uncertainty less than that in the orientations of the specimens along the a and c axes. It is obvious, however, from the figure that the results are consistent among themselves within the limit of experimental error.

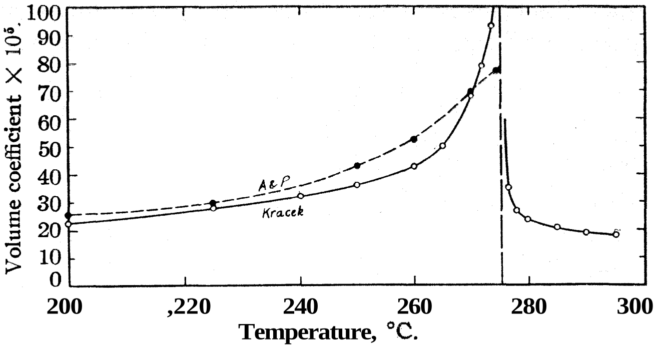

Fig. 4.—Volume expansion coefficient of sodium nitrate: O, Kracek direct determination; ●, Austin and Pierce, calculated from linear expansion coefficients along the crystallographic axes.

It is also possible to calculate the volume expansion of the crystal from the expansions along the directions of the crystallographic axes. Thus the coefficient of cubical expansion β is equal to $\alpha_3 + 2\alpha_1$ where α_3 and α_1 are the linear coefficients in the c direction and *a* directions, respectively. The values of β so calculated are shown by the dotted line in Fig. 4 where they are compared with the direct determinations of Kracek (solid line). The agreement is satisfactory considering the uncertainties inherent in each curve.

It may be worth mentioning in conclusion that our measurements of the temperature at which the transition is completed appeared to be nearer 278° than 275.5° as reported by Kracek. The difference is not serious and may arise from the fact that our temperature measurements were not so precise as his or may possibly be due to different definitions of the completion of the change.

Summary

It has been shown by means of linear expansion measurements in different directions in single crystals of sodium nitrate that the gradual transition occurring between **150** and 278° is most marked in the direction of the *c* axis and was not detected along the a axis. This is interpreted as indicating a separation of the layers of nitrate ions resulting from the change in the eigenfunctions caused by the rotation of the ion. The angle a is calculated to be **45'34'** at 280° as compared with a = **45'35'** obtained from the x-ray data by Kracek, Posnjak and Hendricks.

KEARNY, NEW JERSEY RECEIVED AUGUST 24, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL INSTITUTE OF THE UNIVERSITY OF ROSTOCK]

Anomalous Electrolytes. I. The Electrical Conductivity of Solutions of Iodine and Cyanogen Iodide in Pyridine[1]

BY L. F. AUDRIETH[2] AND E. J. BIRR

It has often been shown that substances which are usually designated as non-electrolytes, with reference to water as solvent, may in suitable media exhibit salt-like properties and yield conducting solutions. This anomalous behavior has been ascribed either to (1) a transformation of a pseudo-salt into a true salt, or (2) to reaction of the solute with the solvent with the resultant formation of solvated compounds of greater or lesser stability which conduct the electric current. Thus nitro compounds have been found to yield conducting solutions in ammonia[3] and in hydrazine,[4] whereas iodine and the cyanogen halides have been found to act as electrolytes in such solvents as liquid sulfur dioxide, arsenious chloride and sulfuryl chloride.[5]

In the first paper of this series the results of a preliminary investigation concerning the nature of solutions of iodine and cyanogen iodide in pyridine, as revealed by a study of their electrical conductivity, are presented.

Experimental

Materials.—The solvent, Pyridin purissimum Kahlbaum, was dried over solid potassium hydroxide and then distilled repeatedly from a solution of cadmium per-

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[1] It is with pleasure that the authors acknowledge their indebtedness to Professor Paul Walden for his interest and encouragement and for his kindness in placing at their disposal the facilities of the laboratory.

[2] University of Illinois, Urbana, Illinois. National Research Council Fellow at the University of Rostock, 1931-1932. The aid of a fellowship grant from the National Research Council, Washington, D. C., is gratefully acknowledged.

[3] Franklin and Kraus, Am. *Chem.* J., *23*, 279 (1900); 27, 191 (1905); Franklin, Z. *physik. Chem.*, *69*, *272* (1909).

[4] Hilgert, Thesis, Rostock, 1932.

[5] Walden, Z *physik. Chem.*, *43*, 385, 409, 423, 445 (1903).

chlorate in an atmosphere free from carbon dioxide and water vapor. The first and final fractions were always rejected. This procedure sufficed to give a highly purified arid anhydrous pyridine whose specific conductivity varied from $\kappa_{25°} = 2.0$ to 7.0×10^{-8}.

Iodine was purified by sublimation from a mixture of pure and dry sodium iodide and iodine. Cyanogen iodide was also purified by sublimation.

Apparatus.—For details of the apparatus employed in carrying out the conductivity measurements reference is made to the original articles.[6] All measurements were carried out at 25°. The conductivity cell which had been employed previously in a study of the conductivity of salts in pyridine[7] was used in the present investigation. The cell constant, $K_c = 0.0824$, was found to have remained unchanged as indicated by a recheck against standard potassium chloride solutions and by comparison with other cells.

(a) Iodine in **Pyridine.**—Iodine dissolves in pyridine to give a brown solution. Addition of water to such a solution, either immediately or after the solution has stood for some time, results in the precipitation of a rather unstable complex compound possessing the formula, $C_5H_5N \cdot I_2$.[8] Since iodine solutions in pyridine are brown, pyridine has been designated as an "active" solvent and one in which "the reactivity (of iodine) is increased by virtue of its coordinative linkage."[9] Thus, iodine in pyridine reacts with silver saccharide to precipitate silver iodide, a reaction which does not take place, or only very slowly, in solvents in which iodine dissolves to give a violet solution.[9]

Both freshly prepared solutions and those which have aged are decolorized by shaking with mercury.

An investigation of such solutions with respect to their electrical conductivity[10] revealed the fact that these undergo rapid change with time. The conductivity increases rapidly during the first hour and then very slowly over a time interval of 100–150 hours. To follow this change more carefully, accurately weighed amounts of iodine were dissolved in pyridine and the change in conductivity with respect to time investigated. Several typical runs are noted in Table I. The concentrations in moles per liter, C, and the dilutions in liters per mole, V, are noted. κ represents the specific conductivity, λ the molecular conductivity calculated on the basis of iodine dissolved as I_2. All values were corrected for the specific conductivity of the solvent, $\kappa_{\text{solv.}}$, which was measured each time before the addition of the iodine. The time in hours is noted.

It is clearly evident from the data in Table I that the character of iodine solutions in pyridine changes profoundly on standing. This fact had already been surmised by Ley and Engelhardt,[11] also by Getman,[12] who

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(6) Walden, Ulich and Birr, *Z physik Chem*, 131, 1 (1927); Ulich, *ibid.*, 115, 377 (1925).

(7) Walden. Audrieth and Birr, *ibid*, [A] 160, 337 (1032).

(8) Waentig, *ibid*, 68, 513 (1910).

(9) Feigl and Bondi, *Monatsh.*, 49, 417 (1928); 53/54, 508 (1929).

(10) Mathews [*J Phys Chem.*, 9, 650 (1905)] reports the specific conductivity of a saturated solution of iodine in pyridine to be $\kappa = 1\ 14 \times 10^{-3}$.

(11) Ley and Engelhardt, *Z. physik Chem*, 74, 55 (1910).

(12) Getman, THIS JOURNAL, 50, 2883 (1028).

TABLE I

CHANGE IN CONDUCTIVITY OF SOLUTIONS OF IODINE IN PYRIDINE WITH TIME, $t = 25°$

(1) $C = 0.0032$, $V = 311$, $\kappa_{\text{solv.}} = 6.9 \times 10^{-8}$			(2) $C = 0.00648$, $V = 154.4$, $\kappa_{\text{solv.}} = 3.34 \times 10^{-8}$		
Time	$\kappa \times 10^{-5}$	X	Time	$\kappa \times 10^{-5}$	λ
0.08	2.453	7.66	0.16	3.58	5.33
.25	4.801	14.98	.33	19.83	30.63
.58	11.3	35.34	.66	20.4	31.5
.83	11.53	35.97	1.00	20.62	31.85
4.42	11.95	37.32	1.33	20.75	32.04
6.00	12.16	37.96	18.33	22.18	34.26
22.00	12.65	39.52	22.00	22.38	34.55
29.76	12.72	39.71	26.75	22.52	34.75
46.9	12.80	39.98	118.0	22.89	35.35

observed a difference in the absorption spectrum of freshly prepared and older solutions of iodine in pyridine.

Since the X-values obtained were extraordinarily high it was deemed advisable to carry out several series of measurements at higher dilutions in order to determine the character of the conductivity curve. The following method was employed.

Stock solutions of iodine in 100 cc. of pyridine were prepared and then kept in a thermostat at 25° for one hundred hours to permit the reaction to come to equilibrium. Fifty cc. of pyridine was then pipetted into the conductivity cell and the specific conductivity of the solvent determined. The various concentrations were then prepared by the addition of definite volumes of stock iodine solution to the solution in the cell. The results of three such series of measurements are presented in Table II in which the molar conductivities, X, and the concentrations, C, are noted.

TABLE II

MOLAR CONDUCTIVITIES OF IODINE SOLUTIONS IN PYRIDINE, $t = 25°$

$C \times 10^{-5}$	λ	$C \times 10^{-5}$	λ
0.0000	132.0	34.38	62.0
4.059	103.5	36.94	59.6
7.814	91.1	42.36	60.7
8.71	90.9	52.9	61.1
16.02	77.1	104.5	53.9
16.77	76.9	224.2	48.4
18.01	73.0	240.8	47.8
22.95	70.5		

At high dilutions a constant conductivity value was quickly attained, but at higher concentrations the solutions revealed a gradual increase toward a constant maximum value. Above dilutions of 5000 liters excellent agreement between the various series of runs was obtained, but with increasing concentrations the final values often showed considerable divergence. The more dilute the original stock solution, the more rapidly were the equilibrium values approached.

By plotting the experimentally determined λ_v-values against the square root of the concentration and extrapolating to infinite dilution (which is permissible since values above 5000 liters lie on a straight line), the surprising value of approximately 130–2 is obtained. This value for the limiting conductivity is about twice as great as might be expected on the basis of a simple dissociation of the iodine molecule into a positive and a negative ion. Such a value might have appeared logical had chemical interaction between solvent and solute resulted in the formation of two molecules of pyridonium iodide, $C_5H_5N{\cdot}HI$, from one molecule of iodine. However, pyridine solutions of iodine, even after standing for a month, still precipitate the insoluble complex, $C_5H_5N{\cdot}I_2$, on the addition of water, and are still largely decolorized by shaking with mercury. Such a reaction can, therefore, not be considered as an explanation for the observed phenomena.

There is only one other possibility and this involves the formation of a ternary electrolyte. In order to explain the experimental findings the following equilibrium must be set up:

$$\mathrm{Py} + \mathrm{I_2} \rightleftharpoons \underset{(\mathrm{A})}{\mathrm{Py{\cdot}I_2}} \rightleftharpoons \underset{(\mathrm{B})}{\mathrm{IPy^+}} + \mathrm{I^-} \rightleftharpoons \underset{(\mathrm{C})}{\mathrm{Py^{++}}} + 2\mathrm{I^-} \qquad (1)$$

$$2[\mathrm{Py{\cdot}I_2}] \rightleftharpoons \underset{(\mathrm{D})}{\mathrm{IPy^+}} + \mathrm{I{\cdot}PyI_2^-} \qquad (2)$$

Equation (I) explains satisfactorily (1), the transformation of the pyridine–iodine complex, a non-electrolyte, into a true salt, *iodipyridonium iodide*[13] (A to B); (2), the extremely labile character of the equilibrium in that the addition of water, and of mercury, drives the reaction to the left with the removal of iodine; (3), the extremely high value for the limiting conductivity, λ_∞, which can only be explained by the formation of a ternary electrolyte (C); (4), the displacement of the equilibrium to the right with decreasing concentration of iodine. Since electrophoresis of such iodine-pyridine solutions (0.02–0.03 *M*) results in the migration of the colored ion to the anode, it is very probable that the transformation of the pseudo-salt involves the intermediate formation of polyiodides, that is, the reaction is a stepwise process as indicated by Equation (2). It is therefore highly probable that solutions of iodine in pyridine contain in equilibrium with one another the various forms A, B, C and D. Dilution shifts this equilibrium to the right with formation of the ternary electrolyte (C), whereas the forms A, B and D predominate in more concentrated solutions.

(b) Cyanogen Iodide in **Pyridine.**—Clark and Streight[14] have already

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(13) In a publication entitled "Über eine neue Klasse von Verbindungen des positiv einwertigen Jods" (Verlag Hirzel, Leipzig, 1932), which has just come to the attention of the authors, Carlsohn describes the preparation and properties of a whole series of salts of the two hypotheticl bases, I(Py)OH and I(Py)OH. Our theory that the rapid change in conductivity of solutions of iodine and cyanogen iodide in pyridine is due to the formation of quaternary iodipyridonium salts is further substantiated by these findings of Carlsohn.

(14) Clark and Streight, Trans. *Roy. Soc. Canada,* [3] **22**, 323 (1928).

shown that solutions of cyanogen iodide in pyridine conduct the electric current. Electrolyses of 0.1 M solutions result in the discharge of cathodic iodine. They ascribe the conductivity of the cyanogen halides to the formation of quaternary pyridonium salts.[14]

An investigation of solutions of cyanogen iodide in pyridine with respect to their electrical conductivity revealed the fact that these too, like the iodine–pyridine solutions, suffered an increase in conductivity on standing. Dilute solutions of cyanogen iodide are at first colorless, but become on standing successively yellow, orange, red-brown and finally deep red-brown. The results of three series of measurements, in which the change in conductivity was observed, are given in Table III.

TABLE III

CHANGE IN CONDUCTIVITY OF SOLUTIONS OF CYANOGEN IODIDE IN PYRIDINE WITH TIME, $t = 25°$

(3) $C = 0.00538$		(4) $C = 0.00352$		(5) $C = 0.00626$	
Time (hrs.)	$\kappa \times 10^{-5}$	Time	$\kappa \times 10^{-5}$	Time	$\kappa \times 10^{-5}$
0.33	0.143	1.00	0.4637	1.58	0.710
.58	.247	1.83	1.109	2.40	1.176
1.00	.456	17.33	7.308	5.00	3.351
3.08	2.212	23.25	7.785	6.83	4.556
4.13	3.72	26.12	7.925	8.00	5.031
5.70	5.67	42.12	8.561	10.66	5.668
7.83	6.245			23.80	7.626
23.83	8.411			29.42	8.186
32.00	8.897			47.00	9.48
50.08	9.74			54.43	9.90
98.83	10.8			72.50	10.81
119.00	11.26			77.70	11.02
				126.00	11.77

The change in conductivity again is due to the formation of an electrolyte. It seems quite probable that a similar sort of reaction mechanism may be postulated for solutions of cyanogen iodide in pyridine as in the case of iodine. However, the transformation of the pseudo-salt into an electrolyte proceeds much more slowly and is further-complicated by side reactions.[15] It is of interest to note that the conductivity values for solutions of cyanogen iodide in pyridine are much lower than those of corresponding concentrations of iodine in this solvent. This fact further supports the formation of an iodipyridonium cyanide,[16] possibly also of a corresponding

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(15) Interaction of pyridine with an ethereal solution of cyanogen bromide results in the formation of an extremely unstable addition compound which can be obtained in crystalline form This substance breaks down rapidly to give a variety of ill-defined decomposition products [Shimidzu. *Chem. Zentr.*, I, **2202** (1927)].

(16) Iodine monochloride also dissolves in pyridine to give a solution whose conductivity increases rapidly upon standing The process of solution is, however, accompanied by very apparent decomposition. It is highly probable that the rapid increase in conductivity may here also be ascribed to the formation of a quaternary pyridonium salt. This assumption is further supported by the fact that the addition of pyridine to a solution of iodine monochloride in ether results in the formation of a crystalline compound, $C_5H_5N\ ClI$ [see Pictet and Krafft, ***Bull. soc.*** chim., [3] 7, **73** (1892)].

ternary electrolyte. Cyanides are much weaker salts in pyridine than are iodides?

Summary

Both iodine and cyanogen iodide dissolve in pyridine to give solutions whose electrical conductivity increases with time to give maximum values The experimental evidence indicates that reaction between solvent and solute results in the primary formation of a non-conducting addition compound which in time changes over to a true quaternary pyridonium salt. In the case of iodine the extraordinarily high value for the molecular conductivity at infinite solution can only be explained by the formation of a ternary salt.

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Electric Moments of Hydrazine and its Derivatives[1]

BY L. F. AUDRIETH,[2] W. NESPITAL AND H. ULICH

In a discussion of the structure of azo compounds as revealed by the measurement of their dipole moments, Bergmann, Engel and Sandor[3] arrive at the conclusion that hydrazo compounds probably also possess a trans-configuration, first, because azotoluene and hydrazotoluene form mixed crystals, and, second, because the former has a zero electric moment and must therefore possess a structure of highest symmetry. While their statement "that only similarly constituted substances can form mixed crystals" is not a question for dispute, it nevertheless seemed highly improbable that a definite comparison between the structures of these two classes of compounds, based on this one observation, was permissible. That hydrazo compounds might easily assume the trans-configuration in solid mixtures in which this form is forced upon it by the symmetry of the other component is very probable. That they should prefer this structure exclusively, say in dilute benzene solution, seemed questionable in view of the fact that the $>$N—N$<$ linkage in hydrazo compounds permits free rotation, that is, theoretically allows a variety of positions of the substituents with respect to each other, whereas the positions of groups in azo compounds with —N=N— linkage is presumably fixed.

That this objection to Bergmann's postulation is correct is conclusively

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[1] The authors acknowledge with pleasure their indebtedness to Professor Paul Walden for his kindness in placing at their disposal the facilities of the laboratory.

[2] University of Illinois, Urbana, Illinois. National Research Council Fellow at the University of Rostock, 1931–1932. The aid of a fellowship grant from the National Research Council, Washington, D. C., is gratefully acknowledged.

[3] Bergmann, Engel and Sandor, *Ber.*, 63,2572 (1930).

proved by our experimental results. Hydrazobenzene possesses an appreciable electric moment, whereas it should have zero moment if it assumed only the trans-configuration, that is, if the substituents were fixed in a position of highest symmetry.

We have also measured the dielectric constants of dilute benzene solutions of hydrazine and several of its derivatives in order to determine the effect of substitution upon the dipole moment of the parent hydronitrogen.

Experimental

Apparatus and Method.—The dielectric constants of the various binary solutions were measured in the apparatus designed and used by Ulich and Nespital,[4] based on the resonance principle and employing a crystal controlled oscillator. For a detailed description of the apparatus and its operation reference is made to the original articles.[4]

The various concentrations were prepared either by the direct addition of the solute to the benzene solution in the condenser cell, or by the preparation of standardized stock solutions in benzene which were pipetted to the solution in the cell. In the latter case an equal amount of solution was always removed from the cell before the addition of the standard solution, so that the volume of liquid remained constant throughout a single series of measurements.

Benzene was used exclusively as the non-polar solvent. Carbon disulfide and carbon tetrachloride had to be eliminated from consideration because of the interaction of these solvents with hydrazine and its derivatives.

All substances were carefully purified either by recrystallization from appropriate solvents, or by distillation under reduced pressure.

Evaluation of the Experimental Data.—The polarization of a binary liquid mixture may be calculated in accordance with Debye[5] from the equation

$$P_{1,2} = P_1X_1 + P_2X_2 = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M_1X_1 + M_2X_2}{d} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M_{1,2}}{d}$$

in which $P_{1,2}$ is *the* molar polarization of the binary liquid mixture; P_1 and P_2, X_1 and X_2, M_1 and M_2, the molar polarizations, mole fractions and molecular weights of the solvent and solute, respectively; ϵ, the dielectric constant of the solution; d, the density of the solution; $M_{1,2}/d$, the average molecular volume of the solution.

The density of the most concentrated solution of each series of measurements was determined and $M_{1,2}/d$ calculated for this concentration. The values for the less concentrated solutions were obtained by interpolation, Only in the case of hydrazine were all $M_{1,2}/d$ values determined by interpo-

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[4] Ulich and Nespital, *Z. physik. Chem.*, **16B**, 227 (1932).

[5] "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929. See also C. P. Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, No. 55, The Chemical Catalog Co., Inc., New York, 1931.

lation between the molecular volumes of pure hydrazine and of pure benzene, assuming a linear variance of $M_{1,2}/d$ with X_2. Where the densities of the pure substances were available, theoretical values for $M_{1,2}/d$ were calculated in the same way and for control compared with those found by direct density measurements.

The molar polarization of the solute, P_2, was calculated on the basis of the above equation in the following form: $P_2 = (P_{1,2} + P_1X_2 - P_1)/X_2$. P_∞ was obtained by extrapolation of the P_2 values to infinite dilution (where $X_2 = 0$). The electric moments were then calculated on the basis of the equation, $\mu = 0.01273 \times 10^{-18} \sqrt{P_M T}$, in which P_M is the polarization due to the permanent moment of the molecule and T, the absolute temperature. P_M was obtained by correcting P_∞ for the induced polarization, $P_E + P_A$, due to deformation of the molecule by the applied electric field. P_E was obtained either by adding together the individual atomic refractivities (D-line) with suitable allowance for variance in type of linkage or, where density and refractive index were available, by application of the Lorenz–Lorentz expression. P_A was arbitrarily taken as 15% of P_E in accordance with the suggestion of K. L. Wolf.[6]

The experimental data[7] are summarized in the tables.

TABLE I

HYDRAZINE,[8] N_2H_4, $t = 18°$

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.002147	2.297	88.52	26.719	83
.00700	2.323	88.24	27.007	85
.007496	2.327	88.21	27.052	86
.008116	2.330	88.18	27.085	87

$P_\infty = 80\text{–}83$

TABLE II

PHENYLHYDRAZINE, $C_6H_5NHNH_2$

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.004061	2.309	88.63	26.925	107
$t = 17.5°$	.008557	2.326	88.68	27.183	95
	.01390	2.351	88.73	27.551	95

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[6] Wolf, *Physik. Z.*, 5, 227 (1930).

[7] The following values for pure benzene were used

t	ϵ	M_1/d	P_1
18°	2.286	88.64	26.597
20°	2.282	88.86	26.605

[8] The anhydrous hydrazine employed had been prepared for use in making conductivity measurements by Dr. H. Hilgert (Thesis, Rostock, 1932). Its specific conductivity was $\kappa_{25°} = 1 \times 10^{-6}$. Due to its slight solubility in benzene, only very dilute solutions could be prepared. The presence of a trace of moisture in the solvent, or exposure of the benzene solution to the air, rapidly caused the solution to become cloudy. In Table I each concentration, X_2, represents a separately prepared stock solution of hydrazine in benzene. Each ϵ-value represents an average of several measurements, each time with fresh portions of the same stock solution.

TABLE II (*Concluded*)

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.003701	2.303	88.63	26.839	93
t = 17.5°	.01226	2.340	88.71	27.389	92
	.02531	2.394	88.84	28.184	90
	.003502	2.301	88.79	26.858	100
t = 19°	.008476	2.320	88.83	27.142	91
	.01646	2.350	88.91	27.592	87

P_∞ = 97–107

TABLE III

α,α-PHENYLMETHYLHYDRAZINE, $C_6H_5(CH_3)NNH_2$, t = 18.5°

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.009341	2.335	88.92	27.384	111
.01475	2.368	89.04	27.886	114
.004733	2.310	88.81	26.994	110
.01028	2.341	88.94	27.475	112
.01751	2.381	89.10	28.087	112

P_∞ = 112

TABLE IV

α,α-DIPHENYLHYDRAZINE, $(C_6H_5)_2NNH_2$, t = 20°

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.003408	2.303	89.08	26.976	136
.007541	2.326	89.40	27.404	133
.01197	2.347	89.71	27.799	126
.004367	2.309	89.17	27.089	137
.01002	2.336	89.57	27.599	126

P_∞ = 141

TABLE V

HYDRAZOBENZENE, $C_6H_5NHNHC_6H_5$, t = 18°

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.000671	2.289	88.69	26.655	113
.002155	2.297	88.79	26.801	121
.005893	2.316	89.06	27.156	121
.001115	2.291	88.72	26.693	113
.003583	2.305	88.90	26.949	124
.009952	2.332	89.35	27.473	115

P_∞ = 117

TABLE VI

BENZALDEHYDE PHENYLHYDRAZONE, $C_6H_5CH{:}NNHC_6H_5$, t = 19°

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.002029	2.297	88.91	26.837	143
.006142	2.327	89.25	27.371	152
.01136	2.362	89.69	28.006	150
.003235	2.309	89.01	27.040	162
.006871	2.334	89.31	27.490	156
.01110	2.362	89.67	27.999	153

P_∞ = 157

TABLE VII

BENZALAZINE, $C_6H_5CH\cdot NN\ CHC_6H_5$, $t = 18°$

X_2	ϵ	$M_{1,2}/d$	P_1,	P_2
0.003585	**2.295**	89.02	26.842	95
.005947	2.300	89 27	26.989	93
01219	2 313	89.93	27.378	91

$P_\infty = 95$

TABLE VIII

ELECTRIC MOMENTS OF HYDRAZINE AND ITS DERIVATIVES

	Substance	P_∞	P_E	$P_E + P_A$[9]	P_M	μ[10]
(1)	Kydrazine	80–83	8 9	10 2	69 8–72 8	1.83–1 85
(2)	Phenylhydrazine	97–107	34 1	39 2	57 8–67 8	1 65–1 79
(3)	α,α-Phenylmethylhydrazine	112	38.6	444	676	1.79
(4)	α,α-Diphenylhydrazine	141	58.3	67.1	73 9	1.87
(5)	Hydrazobenzene	117	58.6	674	496	1.53
(6)	Benzaldehydephenylhydrazone	153	61.4	70.6	82.4	1 **97**
(9)	Benzalazine	95	64 1	73.7	21.3	1 00''

Discussion.—Our values for phenylhydrazine vary somewhat, but if the upper limit is considered as being more nearly the correct one, it is evident that the moments of (2), **(3)** and (4) do not vary greatly from one another and are practically identical with that of hydrazine itself. This result is not at all surprising if one considers that free rotation around the axis of the N—N linkage is possible in hydrazine and those of its derivatives where such rotation is not hampered by the size of the substituent groups. The observed differences may rest in part with the manner in which the P_A values have been approximated. There is reason to assume that hydrocarbon groups give a relatively smaller P_A contribution than has arbitrarily been assigned to them in the above table on the basis of Wolf's suggestion. Consequently, the differences in the dipole moments of the first four substances lie within the limits of the experimental and calculative errors of our method.

That benzaldehyde phenylhydrazone should have a higher moment might also be expected, since it undoubtedly possesses a less symmetrical structure than any of the above substances. If the moment for benzalazine is assumed to be due to the relative positions of the $C_6H_5CH=$ groups, the low moment may be explained as resulting from the fact that the two substituent groups oscillate preferentially in a sector around the trans-position and that, because of the size of these groups, complete rotation around the N—N axis is prevented.[12]

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[9] $P_A = 15\%$ of P_E. See Ref. 6.

[10] In Debye units ($= 10^{-18}$ e. s. u.).

[11] Hassel and Naeshagen, *Tids. Kemi Bergvesen*, 7, 84 (1930), give the value 0.89.

[12] It has been suggested that the presence of the conjugated system may be re-

Summary

The dielectric constants of dilute benzene solutions of hydrazine and several of its derivatives have been measured and their dipole moments calculated.

sponsible for the low electric moment of benzalazine. This possible explanation is. however, somewhat speculative since nothing is known about the effects of such systems.

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Synthetic Glycerides. IV. Esters of Aromatic and Aliphatic Acids

BY DONALD T. JACKSON AND C. G. KING

The general purpose of our investigation has been stated in previous communications.[1] The structural relationships found for fatty acid esters of glycerol have been in agreement with Fischer's[2] findings which showed that methods of preparation which were expected to yield β-monoglycerides gave a-monoglycerides, and that methods which were thought to yield a,β-diglycerides produced a,α'-diglycerides. However, Abderhalden and Eichwald[3] and Bergmann[4] apparently succeeded in preparing α,β-diglycerides of aromatic acids by an indirect and difficult method using propylamines.

Several investigators[6] have continued to use methods which give compounds of different structure than that assigned.[6]

Helferich and Sieber,[7] by the use of triphenylmethyl (trityl) ethers of glycerol, prepared the β-mono-(p-nitrobenzoate) and the β-monobenzoate (probably the first true β-esters of glycerol), and the α,β-dibenzoate.

Bergmann and Carter[8] prepared β-monopalmitin, the first fatty acid ester of this type, by the catalytic reduction of β-palmito-α,α'-benzylidene glycerol.

In the present investigation the β-mono-(p-nitrobenzoate) and the α,β-dibenzoate of glycerol were prepared by the method of Helferich and Sieber and their identity established by their ready conversion, when

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(1) Roche, Averill and King, THIS JOURNAL, 51,866 (1929); 52, 365 (1930); Robinson, Roche and King, *ibid.*, 54,705 (1932).

(2) Fischer, *Ber.*, 53, 1621 (1920).

(3) Abderhalden and Eichwald, *ibid.*, 49, 2095 (1916).

(4) Bergmann, *Z. physiol. Chem.*, 137, 27, 47 (1924).

(5) Heiduschka and Schuster, *J. prakt. Chem.*, 120, 145 (1928); Thomson, *Trans. Roy. Soc. Canada*, 20, 445 (1926); Whitby, *ibid.*, 13, 255 (1919); *J. Chem. Soc.*, 129, 1458 (1926); Delaby and Dubois, *Compt. rend.*, 187, 767 (1928).

(6) Fairbourne, *J. Chem. Soc.*, 372 (1930).

(7) Helferich and Sieber, *Z. physiol. Chem.*, 175, 311 (1928).

(8) Bergmann and Carter, *ibid.*, 191, 211 (1930).

treated with acyl chlorides, into the β-mono-(*p*-nitrobenzoate)-α,α′-dihenzoate (melting point 87°) and the α-mono-(*p*-nitrobenzoate)-α′,β-dibenzoate of glycerol (melting point 113°), respectively. These compounds, to our surprise, were identical with those prepared by Fischer's method (from acetone glycerol). Apparently there was no molecular rearrangement involving the migration of an acyl group in these glycerol esters of aromatic acids. However, when the same reactions were followed through for the preparation of 8-monopalmitin, β-monostearin, α,β-dipalmitin and α,β-distearin, the only products which could be identified were the a-monoglycerides in the first case, and the symmetrical diglycerides in the second case. The symmetrical aromatic ester also melted lower than the unsymmetrical isomer, reversing the order for aliphatic esters. This peculiarity appears to be characteristic of the esters with one *p*-nitrobenzoate group.[9]

Experimental

The α,α′-ditrityl and a!-monotrityl ethers of glycerol were prepared essentially as described by Helferich and co-workers, having melting points of 176° and 108–110°, respectively.

Preparation of **α,α′-Ditrityl** Ether of **β-Monopalmitin.**—To a solution of 5 7 g. of symmetrical ditrityl ether of glycerol dissolved in 20 cc. of dry benzene and 3 cc. of quinoline, there was added a mixture of 3 g. of palmityl chloride and 3 cc. of quinoline. This mixture was kept at 40° for eighty-four hours, by which time a heavy white precipitate of quinoline hydrochloride had settled out. The mixture was taken up in 50 cc. of benzene and 50 cc. of half-normal sulfuric acid, washed several times with half-normal sulfuric acid, then with 10% potassium bicarbonate solution and finally with water. After drying over sodium sulfate, the benzene was evaporated at room temperature. The sirup which remained was taken up in acetone and poured into anhydrous alcohol. A precipitate formed which, after several recrystallizations from acetone and alcohol, melted at 71.5°, yield 5.6 g.

The α,α′-ditrityl ethers of 6-monostearin, m. p. 78.5–79.5°, β-mono-(*p*-nitrobenzoate), m. p. 187.5" and β-monolaurin, m. p. 47°, were prepared in a similar manner.

Preparation of Monotrityl Derivatives.—The α-monotrityl ethers of a, β-dipalmitin, melting point 40.5–41.5°, of α,β-distearin, melting point 46–48°, and of α,β-dibenzoate of glycerol, melting point 92–94°, were prepared according to the method which is described for the preparation of the a-monotrityl ether of α,β-dipalmitin. A mixture of 11.2 g. of palmityl chloride and 5 cc. of quinoline was added to a solution of 6.7 g. of glycerol monotrityl ether dissolved in 20 cc. of benzene and 5 cc. of quinoline. The reaction mixture, after standing at 35–40' for twenty-four hours, was taken up in benzene, washed with cold half-normal sulfuric acid, then with 10% potassium bicarbonate solution and dried over sodium sulfate. The product was crystallized by evaporation of the benzene and recrystallized from acetone–alcohol mixture; melting point 40.5–41.5°; yield 40%.

Removal of Trityl Groups.—The following procedure for the removal of the trityl groups from α,α′-ditrityl ether of β-monopalmitin was used for all compounds of this type. A solution of 5 g. of the ditrityl ether of β-monopalmitin was shaken for one hour at 0° with 15 cc. of a chloroform solution saturated at 0° with hydrogen bromide. Any triphenylmethyl bromide which separated was filtered off. The filtrate was washed with

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(9) *Ber.*, **53**, 1596 (1920); *ibid.*, 54, 936 (1921).

potassium bicarbonate solution and with water, dried over sodium sulfate, and the solvent evaporated. The residue was taken up in acetone, petroleum ether was added and the solution allowed to stand. Crystals of triphenylcarbinol (from the hydrolysis of triphenylmethyl bromide) soon appeared and were filtered off. The a-monopalmitin crystallized out after evaporating part of the solvent and cooling.

Molecular weights were determined for all of the new compounds and most of the intermediates used in their preparation, using the method of Menzies and Wright,[10] with ethyl acetate as the solvent.

Summary

The β-mono-(*p*-nitrobenzoate) and the α,β-dibenzoate of glycerol have been prepared from glycerol trityl ethers and found to correspond to the compounds previously prepared by Helferich and Sieber. These compounds, when thus prepared, apparently do not undergo a rearrangement involving the migration of the aromatic acyl group. The same procedures when used for the preparation of β-monopalmitin, β-monostearin, α,β-dipalmitin and α,β-distearin resulted in the migration of the aliphatic acyl groups and the production of the isomeric a-monoglycerides and α,α′-diglycerides.

The synthesis and identification of the following compounds has been described: the α,α′-ditrityl ether of β-monostearin, the a,α′-ditrityl ether of β-monolaurin, the a-monotrityl ether of α,β-dipalmitin, the a-monotrityl ether of α,β-distearin, and the a-monotrityl ether of acetoneglycerol.

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[10] Menzies and Wright, THIS JOURNAL, 43, 2314 (1921).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

The Number of Structurally Isomeric Hydrocarbons of the Ethylene Series[1]

BY HENRY R. HENZE AND CHARLES M. BLAIR

The method for calculating the number of structural isomers by establishing a unique relationship between the number of structurally isomeric hydrocarbons of the methane series and of the acetylene series and the alkyl groups of which these may be considered to be composed may also be utilized successfully in calculating the number of structurally isomeric hydrocarbons of the ethylene series.

The homologs of ethylene are divided into four groups: A, consisting of those hydrocarbons which may be formed, theoretically, by replacing one hydrogen atom of ethylene by an alkyl radical; B, in which two hydrogen atoms are replaced by alkyl groups; C, in which three hydrogen atoms are replaced by alkyls; and D, in which all four hydrogen atoms are replaced.

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[1] This paper was presented before the Central Texas Section of the American Chemical Society at its annual meeting in Waco, Texas, on April 23, 1932. Previous contributions in this series are Henze and Blair, THIS JOURNAL, 53, 3042–3046, 3077–3085 (1931); 54, 1098-1106, 1538–1545 (1932); Coffman, Blair with Henze, *ibid.*, 55, 252-253 (1933).

Group A.—The total number of structural formulas of olefin hydrocarbons of N carbon atom content included in Group A, $CH_2{=}CHR$, and formed by replacing one hydrogen atom in ethylene by an alkyl radical of $N - 2$ carbon atom content, will equal the total number of such alkyl radicals[2] or $T_{(N-2)}$.

$$A_N = T_{(N-2)} \tag{A}$$

Group **B.**—The structural formulas of the hydrocarbons of Group B are theoretically of two types: (1), those in which the alkyl radicals, R- and R'- (the carbon content of R- plus R'- always equaling $N-2$), are of unequal carbon content; and (2), in which the alkyls are of equal carbon content. Type (2) is actually impossible with hydrocarbons of uneven carbon content for in this type N—2 should be divisible by two. Each of the types (1) and (2) may be further divided into two subtypes: (a), in which the two alkyl radicals are attached to the same carbon atom of the ethylene group, $H_2C{=}CRR'$; and (b), in which the alkyls are not attached to the same carbon atom, $RHC{=}CHR'$. Derivation of (finite) recursion formulas for calculating the number of isomeric hydrocarbons of odd carbon atom content included, respectively, in subtypes (a) and (b) leads to identical expressions Hence twice the number calculated by means of that formula equals the total number of isomeric homologs of ethylene included in Group B. An analogous relationship exists between subtypes (a) and (b) of the hydrocarbons of even carbon atom content. The following represent such formulas for odd and even carbon atom contents, respectively

Odd:

$$B_N = 2[T_1{\cdot}T_{(N-3)} + T_2{\cdot}T_{(N-4)} + \dots T_{(N-3)/2}{\cdot}T_{(N-1)/2}] \tag{B$_o$}$$

Even:

$$B_N = 2\left[T_1{\cdot}T_{(N-3)} + T_2{\cdot}T_{(N-4)} + \dots T_{(N-4)/2}{\cdot}T_{N/2} + \frac{T_{(N-2)/2}{\cdot}(1 + T_{(N-2)/2})}{2}\right] \tag{B$_e$}$$

Note that the subscripts in each term add up to N—2, and that the number of terms is $(N-3)/2$ for odd carbon content and $(N-2)/2$ for even.

Group C.—The structural formulas of the hydrocarbons included in Group C are theoretically of three types: (1), those in which the alkyl radicals, R-, R′- and R″- (the carbon content of R- plus R′- plus R″- always equaling N—2), are of different carbon content; (2), those in which two of the alkyl radicals, R- and R′- are of equal carbon content and different from that of the third, R″-; and (3), those in which all three alkyls are of the same carbon content. Type (3) is actually possible only when $(N-2)/3$ is an integer.

Type (1) may be further divided into three subtypes: (a), in which the alkyl radicals R- and R'- are attached to the same carbon atom of the ethylene group, $RR'C{=}CHR''$; (b), in which R- and R″- are attached

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[2] For the total number of alkyl radicals, which are, of course numerically equal to the number of structurally isomeric alcohols of the methanol series, through C_{20} see THIS JOURNAL, 63, 3045 (1931).

to the same carbon atom, $RR''C{=}CHR^1$; and (c), in which R'- and R''- are attached to the same carbon atom, $R'R''C{=}CHR$. Derivation of (finite) recursion formulas for calculating the number of isomeric hydrocarbons included in subtypes (a), (b) and (c) leads to identical expressions. Hence the total number of isomers included in type (1) will equal three times the number calculated by that expression for each subtype or

$$3\Sigma T_i \cdot T_j \cdot T_k \tag{C$_1$}$$

where i, j and k are integers, distinct, and greater than zero; $i + j + k = N - 2$; $i > j > k$.

Type (2) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom of the ethylene group, $RRC{=}CHR^1$; and (b), in which the two alkyls of equal carbon content are not attached to the same carbon atom, $RR'C{=}CHR$. The number of isomers included in subtype (a) equals $1/2\Sigma T_i \cdot T_j \cdot (1 + T_i)$. The number of isomers in subtype (b) equals $\Sigma(T_i)^2 \cdot T_j$. Hence, the total number of isomeric homologs of ethylene included in type (2) may be calculated by use of a summation of these two expressions, or

$$1/2\Sigma T_i \cdot T_j \cdot (1 + 3T_i) \tag{C$_2$}$$

where i and j are integers, distinct, and greater than zero, and $2i + j = N - 2$.

The total number of isomers of type (3) is given by the expression

$$1/2\Sigma (T_i)^2 \cdot (1 + T_i) \tag{C$_3$}$$

where i is an integer greater than zero, and $3i = N - 2$.

Group D.—The structural formulas of the hydrocarbons included in group D are theoretically of five types: (1), those in which the four alkyls R-, R'-, R''- and R'''- are of different carbon content; (2), those in which two of the alkyl radicals are of equal carbon content and each of the others, R'- and R''-, of different carbon content; (3), those in which three of the alkyl radicals are of the same carbon content and different from that of the fourth, R'-; (4), those in which all four alkyls are of the same carbon content; and (5), those in which the four alkyl radicals can be divided into two sets of two each, the individual members of each set being of the same carbon content but differing in carbon content from the members of the other set. It will be seen that types (4) and (5), though theoretically possible for hydrocarbons of both odd and even carbon content, are actually possible only for the latter, for in type (4) $N-2$ should be divisible by four, and in type (5) $N-2$ should be divisible by two.

Type (1) may be further divided into three subtypes: (a), in which the alkyl radicals R- and R'- are attached to the same carbon atom of the ethylene group, $RR'C{=}CR''R'''$; (b), in which R- and R''- are attached to the same carbon atom, $RR''C{=}CR'R'''$; and (c), in which R- and R'''- are attached to the same carbon atom, $RR'''C{=}CR'R''$. Here, again, the expression for the number of isomers in subtype (a) is identical with that for (b) and for (c), hence the total number of isomeric homologs of ethylene of type (1) is given by the formula

$$3\Sigma T_h\cdot T_i\cdot T_j\cdot T_k \tag{D$_1$}$$

where h, i, j and k are integers, distinct, and greater than zero; $h + i + j + k = N - 2$; and $h > i > j > k$.

Type (2) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom of the ethylene group, RRC═CR′R″; and (b), in which the two alkyl radicals of equal carbon content are not attached to the same carbon atom, RR′C═CR″R. The number of isomers included in subtype (a) equals $1/2\Sigma T_i\cdot T_j\cdot T_k\cdot(1 + T_i)$. The number of isomers in subtype (b) equals $\Sigma(T_i)^2\cdot T_j\cdot T_k$. Hence, the total number of isomeric homologs of ethylene included in type (2) is equal to the sum of these expressions, or

$$1/2\Sigma T_i\cdot T_j\cdot T_k\cdot(1 + 3T_i) \tag{D$_2$}$$

where i, j and k are integers, distinct, and greater than zero; $2i + j + k = N - 2$; and $j > k$.

The total number of isomers of type (3) is given by the expression

$$1/2\Sigma(T_i)^2\cdot T_j\cdot(1 + T_i) \tag{D$_3$}$$

where i and j are integers, distinct, and greater than zero; and $3i + j = N - 2$.

The number of isomers of type (4) may be calculated by use of the formula

$$1/8\,[T_i\cdot(1 + T_i)][2 + T_i\cdot(1 + T_i)] \tag{D$_4$}$$

where i is an integer greater than zero, and $4i = N - 2$.

Type (5) may be further divided into two subtypes: (a), in which the two alkyl radicals of equal carbon content are attached to the same carbon atom, RRC═CR′R′, and (b), in which the two alkyl radicals of equal carbon content are not so attached, RR′C═CR′R. The total number of homologs of ethylene of type (5), including both subtypes (a) and (b), may be calculated by the following (finite) recursion formula

$$1/4\Sigma T_i\cdot T_j\cdot(3T_i\cdot T_j + 3 + T_i + T_j) \tag{D$_5$}$$

where i and j are integers, distinct, and greater than zero; $2i + 2j = N - 2$; $i > j$.

In Table I is to be found a summary of the number of terms actually present in all theoretically possible cases of Groups A, B, C and D through a carbon content of forty. Since the number of alkyl groups through C_{20} is recorded in a previous contribution, it is now possible to calculate the number of structurally isomeric hydrocarbons of the ethylene series through a-carbon content of twenty-two. Hence, to calculate the total number of structurally isomeric hydrocarbons of this series of higher carbon content it would be necessary to make a preliminary calculation of the total number of alkyl radicals (structurally isomeric monosubstitution products of the paraffins) of N—2 and all lesser carbon contents.

TABLE I

NUMBER OF TERMS IN ALL THEORETICALLY POSSIBLE CASES

Carbon content	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
A	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C_1				1	2	4	7	10	14	19	24	30	37	44	52	61	70	80	91	102
C_2			1	1	3	4	4	6	7	7	9	10	10	12	13	13	15	16	16	18
C_3				1			1			1			1			1			1	
D_1						1	2	5	9	15	23	34	47	64	84	108	136	169	206	249
D_2					2	3	8	11	17	23	31	38	49	58	70	82	96	109	126	141
D_3				1	1	3	2	4	4	5	5	7	6	8	8	9	9	11	10	12
D_4			1		1		1		1		1		1		1		1		1	
D_5				1	1	2	2	3	3	4	4	5	5	6	6	7	7	8	8	9
Total	1	2	5	9	15	23	34	47	64	84	108	136	169	206	249	297	351	411	478	551

Carbon content	3	5	7	9	11	13	15	17	19	21	23	25	27	29	31	33	35	37	39	41
A	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
H		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C_1				1	3	5	8	12	16	21	27	33	40	48	56	65	75	85	96	108
C_2			2	3	3	5	6	6	8	9	9	11	12	12	14	15	15	17	18	18
C_3		1			1			1			1			1			1			1
D_1						1	3	6	11	18	27	39	54	72	94	120	150	185	225	270
D_2				1	4	7	11	17	23	30	39	48	58	70	82	95	110	125	141	159
D_3			1	2	2	3	4	4	5	6	6	7	8	8	9	10	10	11	12	12
Total	1	3	6	11	18	27	39	54	72	94	120	150	185	225	270	321	378	441	511	588

The total number of structurally isomeric alkenes of N carbon atoms may be obtained by a summation of the numbers calculated in Groups A, B, C and D. The actual meaning and use of these recursion type formulas may be illustrated in the calculation of the number of structurally isomeric tetradecylenes, since the hydrocarbons corresponding to $C_{14}H_{28}$ represent the simplest homologs of ethylene in which all structural types are represented.

SAMPLE CALCULATION

Group A. $N = 14;\ N - 2 = 12$

$T_{(N-2)} = 3057$

Group B. Even carbon content; number of terms is $(N - 2)/2 = 6$

$$2 \cdot T_1 \cdot T_{11} = 2 \cdot 1 \cdot 1238 = 2476$$
$$2 \cdot T_2 \cdot T_{10} = 2 \cdot 1 \cdot 507 = 1014$$
$$2 \cdot T_3 \cdot T_9 = 2 \cdot 2 \cdot 211 = 844$$
$$2 \cdot T_4 \cdot T_8 = 2 \cdot 4 \cdot 89 = 712$$
$$2 \cdot T_5 \cdot T_7 = 2 \cdot 8 \cdot 39 = 624$$
$$2 \cdot \frac{T_6 \cdot (1 + T_6)}{2} = 2 \cdot \frac{17 \cdot 18}{2} = 306$$

Group C.

Type (1)

$$3\,T_9\,T_2\,T_1 = 3\cdot 211\cdot 1\cdot 1 = 633$$
$$3\,T_8\,T_3\,T_1 = 3\cdot 89\cdot 2\cdot 1 = 534$$
$$3\,T_7\cdot T_4\,T_1 = 3\cdot 39\cdot 4\cdot 1 = 468$$
$$3\,T_7\cdot T_3\cdot T_2 = 3\cdot 39\cdot 2\cdot 1 = 234$$
$$3\cdot T_6\cdot T_5\cdot T_1 = 3\cdot 17\cdot 8\cdot 1 = 408$$
$$3\cdot T_6\cdot T_4\cdot T_2 = 3\cdot 17\cdot 4\cdot 1 = 204$$
$$3\cdot T_5\cdot T_4\cdot T_3 = 3\cdot 8\cdot 4\cdot 2 = 192$$

Type (2)

$$1/2\,T_1\cdot T_{10}\,(1 + 3T_1) = 1/2\cdot 1\cdot 507\,(1 + 3\cdot 1) = 1014$$
$$1/2\cdot T_2\cdot T_8\cdot(1 + 3T_2) = 1/2\cdot 1\cdot 89\cdot(1 + 3\cdot 1) = 178$$
$$1/2\cdot T_3\cdot T_6\cdot(1 + 3T_3) = 1/2\cdot 2\cdot 17\cdot(1 + 3\cdot 2) = 119$$
$$1/2\cdot T_5\cdot T_2\cdot(1 + 3T_5) = 1/2\cdot 8\cdot 1\cdot(1 + 3\cdot 8) = 200$$

Type (3)

$$1/2\cdot(T_4)^2\cdot(1 + T_4) = 1/2\cdot 4^2\cdot(1 + 4) = 40$$

Group D.

Type (1)

$$3\cdot T_6\,T_3\cdot T_2\cdot T_1 = 3\cdot 17\cdot 2\cdot 1\cdot 1 = 102$$
$$3\cdot T_5\cdot T_4\cdot T_2\cdot T_1 = 3\cdot 8\cdot 4\cdot 1\cdot 1 = 96$$

Type (2)

$$1/2\cdot T_1\,T_8\,T_2\,(1 + 3T_1) = 1/2\cdot 1\cdot 89\cdot 1\cdot(1 + 3\cdot 1) = 178$$
$$1/2\cdot T_1\cdot T_7\,T_3\cdot(1 + 3T_1) = 1/2\cdot 1\cdot 39\cdot 2\,(1 + 3\cdot 1) = 156$$
$$1/2\cdot T_1\,T_6\cdot T_4\,(1 + 3T_1) = 1/2\cdot 1\cdot 17\cdot 4\cdot(1 + 3\cdot 1) = 136$$
$$1/2\cdot T_2\cdot T_7\cdot T_1\cdot(1 + 3T_2) = 1/2\cdot 1\cdot 39\cdot 1\cdot(1 + 3\cdot 1) = 78$$
$$1/2\cdot T_2\cdot T_5\cdot T_3\cdot(1 + 3T_2) = 1/2\cdot 1\cdot 8\cdot 2\cdot(1 + 3\cdot 1) = 32$$
$$1/2\cdot T_3\cdot T_5\,T_1\cdot(1 + 3T_3) = 1/2\cdot 2\cdot 8\cdot 1\cdot(1 + 3\cdot 2) = 56$$
$$1/2\cdot T_3\cdot T_4\cdot T_2\cdot(1 + 3T_3) = 1/2\cdot 2\cdot 4\cdot 1\cdot(1 + 3\cdot 2) = 28$$
$$1/2\cdot T_4\cdot T_3\cdot T_1\cdot(1 + 3T_4) = 1/2\cdot 4\cdot 2\cdot 1\cdot(1 + 3\cdot 4) = 52$$

Type (3)

$$1/2\,(T_1)^2\cdot T_9\,(1 + T_1) = 1/2\cdot 1^2\cdot 211\cdot(1 + 1) = 211$$
$$1/2\cdot(T_2)^2\cdot T_6\,(1 + T_2) = 1/2\cdot 1^2\cdot 17\cdot(1 + 1) = 17$$

Type (4)

$$i = (n - 2)/4 = (14 - 2)/4 = 3$$
$$1/8\,T_3\,(1 + T_3)\cdot[2 + T_3\,(1 + T_3)] = 1/8\cdot 2\,(1 + 2)\,[2 + 2\,(1 + 2)] = 6$$

Type (5)

$$1/4\,T_5\cdot T_1\cdot(3\cdot T_5\,T_1 + T_5 + T_1 + 3) = 1/4\cdot 8\cdot 1\,(3\cdot 8\cdot 1 + 8 + 1 + 3) = 72$$
$$1/4\cdot T_4\cdot T_2\,(3\,T_4\cdot T_2 + T_4 + T_2 + 3) = 1/4\cdot 4\cdot 1\cdot(3\cdot 4\cdot 1 + 4 + 1 + 3) = 20$$

Thus, of the tetradecylenes there are 14,497 structural isomers. The totals of such structural isomers, as obtained by the use of these recursion formulas, through a carbon content of twenty are shown in Table II.[3]

TABLE II

NUMBER OF STRUCTURALLY ISOMERIC HYDROCARBONS OF THE ETHYLENE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers	Carbon content	Number of isomers
2	1	9	153	15	36,564
3	1	10	377	16	93,650
4	3	11	914	17	240,916
5	5	12	2,281	18	623,338
6	13	13	5,690	19	1,619,346
7	27	14	14,497	20	4,224,993
8	66				

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(3) The structural formulas of the homologs of ethylene, inclusive of a carbon content of eleven, were written in connection with the derivation of these recursion formulas. The totals obtained from actual count of these structural formulas agreed exactly with those derived by use of the recursion formulas

Summary

By means of a separation of the isomeric hydrocarbons of the ethylene series of each specified carbon content into types, arbitrarily chosen upon the basis of their structural formulas, a relationship may be established between the number of structurally isomeric homologs of ethylene and the alkyl groups which may be considered to be attached to the $>C=C<$ grouping. Mathematical formulas of the (finite) recursion type are advanced which permit of the calculation, from their carbon content, of the number of isomers in each of these structural types. In using these recursion formulas to calculate the total number of such structurally isomeric hydrocarbons of any given carbon content, the total number of alkyl groups (*i. e.*, the total number of structurally isomeric monosubstitution products of the paraffins) of N—2 and all lesser carbon contents must be known.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Naphthol Studies. II. The Chlorination of 1,5-Dihydroxynaphthalene

BY ALVIN S. WHEELER AND W. J. MATTOX[1]

The studies of Wheeler and Ergle[2] have shown that one, two or three atoms of bromine may be introduced into 1,5-dihydroxynaphthalene. In the present study we have prepared dichloro and trichloro derivatives but no tetrachloro compound was obtained. A similar relation was noted in the juglone studies of Wheeler and co-workers,[3,4] more bromine being taken up than chlorine. Willstatter and Schuler[5] chlorinated dihydroxynaphthalene in acetic acid solution but for the purposes of this study we found it better to chlorinate the diacetate in carbon tetrachloride. The description of our compounds C and G does not agree with that of Willstatter and Schuler. This will be re-examined, In chlorinating the diacetate at room temperature two atoms of chlorine are taken up whereas at 80° three atoms are introduced. In each case one acetyl group is hydrolyzed. We tried to prove that OH and O in compound I are ortho to each other by Dimroth's pyroboroacetate ester method. We obtained the characteristic reddish purple color but no solid product. The first two chlorine atoms are put in positions 4 and 8 and the third also in 4 since one

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(1) Extract from a thesis presented to the Faculty of the University of North Carolina by W. J. Mattox for the degree of Doctor of Philosophy in 1932.

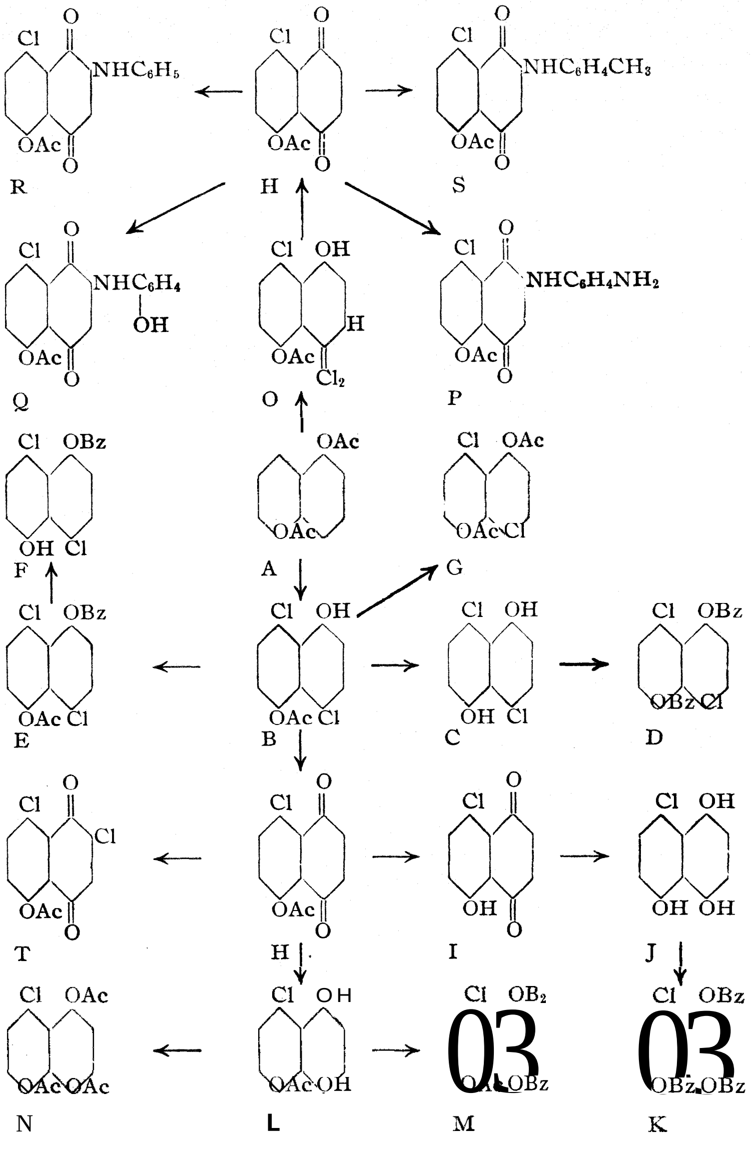
(2) Wheeler and Ergle, THIS JOURNAL, 52, 4873 (1930).

(3) Wheeler and Scott, *ibid.*, 41, 834 (1919).

(4) Wheeler, Dawson and McEwen, *ibid.*, 45, 1970 (1923).

(5) Willstatter and Schuler, Ber., 61, 362 (1928).

O replaces 2Cl in the production of compound H. This is in harmony with the observed instability of compound O. Quinone H gave characteristic reactions with several aromatic amines. The nitroanilines, sulfanilic acid, *p*-aminobenzoic acid and 2,4-dichloroaniline did not react.



Experimental

4,8-Dichloro-1-hydroxy-5-acetoxynaphthalene (B).—Five grams of the diacetate of 1.5-dihydroxynaphthalene (m. p. 159°) was suspended in 40 cc. of carbon **tetra-**

chloride, a small crystal of iodine was added and a slow stream of chlorine passed at room temperature until solution took place. The solution after treatment with charcoal was reduced one-half in volume in a vacuum desiccator. Petroleum ether was then added until a cloudiness remained after stirring. The colorless needles which soon separated were recrystallized from a small amount of glacial acetic acid. On heating the substance it turned green at 158–160° and then effervesced vigorously. If recrystallized from alcohol yellow impurities clung tenaciously to the crystals. The product was soluble in acetone, chloroform and ether.

Anal. Calcd. for $C_{12}H_8O_3Cl_2$: Cl, 26.19. Found: Cl, 26.34.

4,8-Dichloro-1,5-dihydroxynaphthalene (C).—Compound B may be hydrolyzed in alkaline or acid solution, but the acid hydrolysis is to be preferred. The alkaline solution is purple in color and acidification gives a greenish product. The acid hydrolysis gives at once a white product. Two grams was dissolved in 100 cc. of warm alcohol and 30 cc. of concd. hydrochloric acid was added. The solution after standing four to five hours was poured into 200 cc. of water. The white precipitate was recrystallized from glacial acetic acid as fine, colorless needles, m. p. 194". Willstatter and Schuler give 188–189° for a pale yellow product. The compound is soluble in alcohol, ether, chloroform, hot benzene and carbon tetrachloride. It darkens slowly on exposure to light and air.

Anal. Calcd. for $C_{10}H_6O_2Cl_2$: Cl, 31.00. Found: Cl, 30.75.

8-Chloro-5-acetoxy-1,4-naphthoquinone (H).—Two grams of B was dissolved in 40 cc. of glacial acetic acid at 50° and a solution of 4 g. of chromic acid in 10 cc. of water was added. After standing for two to three hours the solution was poured into several volumes of water. The precipitated quinone was dissolved in acetone and warmed with charcoal. The filtered solution was mixed with water, giving fine yellow needles, m. p. 143". It can be recrystallized from alcohol in a yield 45%. This quinone was also obtained by the oxidation of the trichloro compound O. It is stable and sublimes without decomposition.

Anal. Calcd. for $C_{12}H_7O_4Cl$: Cl, 14.17. Found: Cl, 14.32

4,4,8-Trichloro-1-hydroxy-5-acetoxynaphthalene (O).—Five grams of A was dissolved in 25 cc. of glacial acetic acid. Chlorine was passed into the solution at 50° for two and one-half hours. The solution became red and on cooling with ice the trichloro compound crystallized out. Sometimes seeding was necessary. The color of the crystals was largely removed by washing with petroleum ether. Kccrystallization from hot glacial acetic acid gave colorless needles, m. p. 174°, yield 2.5 g.; soluble in acetone, hot alcohol, ether and benzene. The substance darkens in a few days when exposed to sunlight. It is readily decomposed by dilute alkali. Boiling for several hours with absolute alcohol does not remove any chlorine. Oxidation in glacial acetic acid with chromic acid gives the quinone H as does also the compound B.

Anal. Calcd. for $C_{12}H_9O_3Cl_3$: Cl, 34.75. Found: Cl, 34.72.

The dichloro compound B also takes up chlorine at 80° giving the same compound O. Analysis for Cl gave 34.69.

2,8-Dichloro-5-acetoxy-1,4-naphthoquinone (T).—One-half gram of H was dissolved in 10 cc. of glacial acetic acid and an excess of chlorine passed into the solution Water was added until a faint cloudiness appeared The product crystallized out on standing. It was recrystallized from alcohol as pale yellow needles, m. p. 158–159°. It is noteworthy that only one atom of chlorine is taken up.

Anal. Calcd. for $C_{12}H_6O_4Cl_2$: Cl, 24.91. Found: Cl, 24.37.

In the table other derivatives are indicated.

TABLE I

	Compound	Source	Reagent	Cryst. solvent	M. p., °C.	Solubilities			Formula	Cl, %	
						Alc.	C_6H_6	Gl. ac.		Calcd.	Found
D	4,8-Dichloro-1,5-dibenzoxynaphthalene	B	PhCOCl	Acetone	179	..	..	..	$C_{19}H_{12}O_4Cl_2$	18.90	18.75
F	4,8-Dichloro-1-benzoxy-5-hydroxynaphthalene	E	Alc. + HCl	Gl. AcOH	157–158	..	..	..	$C_{17}H_{10}O_2Cl_2$	21.14	21.32
G	4,8-Dichloro-1,5-diacetoxynaphthalene	B	CH_3COCl	Acetone	143	SS	SS	SS	$C_{14}H_{10}O_4Cl_2$	22.66	22.81
I	8-Chloro-5-hydroxy-1,4-naphthoquinone	H	Alc. + HCl	Alc.	112	S	S	S	$C_{10}H_5O_3Cl$	17.01	16.95
J	8-Chloro-1,4,5-trihydroxynaphthalene	I	$SnCl_2$	Dil. alc.	115–120 dec.	S	S	S	$C_{10}H_7O_3Cl$	16.85	16.54
K	8-Chloro-1,4,5-benzoxynaphthalene	J	PhCOCl	Xylene	210	i	i	i	$C_{31}H_{19}O_6Cl$	6.79	6.92
L	8-Chloro-1,4-dihydroxy-5-acetoxynaphthalene	H	Zn + dil. H_2SO_4	Gl. AcOH	173 dec.	..	..	S	$C_{12}H_9O_4Cl$	14.05	13.98
M	8-Chloro-1,4-dibenzoxy-5-acetoxynaphthalene	L	PhCOCl	Gl. AcOH	216	SS	SS	S	$C_{26}H_{17}O_6Cl$	7.70	7.56
N	8-Chloro-1,4,5-triacetoxynaphthalene	L	Ac_2O	Gl. AcOH	147	SS	S	S	$C_{16}H_{12}O_6Cl$	10.54	10.69
P	8-Chloro-5-acetoxy-1,4-naphthoquinone-*o*-aminoanilide	H	$C_6H_4(NH_2)_2$	....	271 dec.	i	i	i	$C_{18}H_{13}O_4N_2Cl$	9.96	10.39
Q	8-Chloro-5-acetoxy-1,4-naphthoquinone-*p*-hydroxyanilide	H	$C_6H_4OHNH_2$-*p*	....	226 dec.	S	S	S	$C_{18}H_{12}O_5NCl$	9.93	9.53
R	8-Chloro-5-acetoxy-1,4-naphthoquinone anilide	H	$C_6H_5NH_2$	....	172	S	S	S	$C_{18}H_{12}O_4NCl$	10.33	10.45
S	8-Chloro-5-acetoxy-1,4-naphthoquinone-*p*-methylanilide	H	$C_6H_4CH_3NH_2$-*p*	....	169	S	S	S	$C_{19}H_{14}O_4NCl$	9.98	10.06

Summary

1. 1,5-Diacetoxynaphthalene suspended in carbon tetrachloride yields with chlorine in the sunlight or with iodine as a catalyst a dichloro substitution product and at 80° a trichloro product.

2. The chloro compounds yield the same quinone when oxidized with chromic acid.

3. The quinone gave mono, di and trihydroxy naphthols.

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The Reaction between Alpha, Beta-Unsaturated Ketones and Organic Magnesium Compounds. Unsaturated Mesitylenic Ketones

BY E. P. KOHLER AND CARL E. BARNES

Earlier papers on this subject contain a description of the reaction between organic magnesium compounds and every member of the series of alpha, beta-unsaturated ketones which could be formed by replacing the hydrogen atoms in acrolein one by one with phenyl groups. Not one of these ketones under any conditions formed a product containing more than two phenyl groups in the beta position. In the case of tetraphenyl propenone, from which such a product was most to be expected, the reaction took an entirely unexpected direction involving addition to a phenyl group.[1]

$$(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)COC_6H_4C_6H_5(o)$$

In view of this result it now became a matter of interest to study the reaction with unsaturated mesitylenic ketones which are so constituted that the hindrance to 1,2 addition would be prohibitive, and that any type of 1,4 addition would inevitably lead to substances with three hydrocarbon residues in the β-position. With this end in view we decided to investigate the behavior of beta phenyl benzalacetomesitylene. The reaction between phenylmagnesium bromide and this ketone had been briefly examined many years ago with negative results,[2] but with the experience gained since then in working with highly phenylated compounds this outcome no longer seemed inevitable.

We have now found that by operating under favorable conditions and with sufficient persistence it is possible to add both phenylmagnesium bromide and ethylmagnesium bromide to this ketone in ether. In the case of methylmagnesium iodide the highly colored intermediate complex product is so nearly insoluble in ether that a reaction in this solvent is impossible but even here it is possible to secure reaction by operating at a

[1] Kohler and Nygaard, THIS JOURNAL, **52**, 4128 (1930).

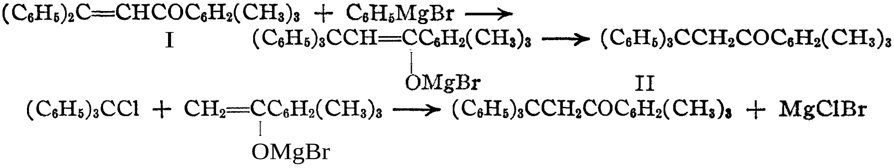
[2] Kohler, Am. *Chem.* J., 38, 560 (1907).

higher temperature in benzene. In all three cases the products are saturated ketones.

These highly substituted saturated ketones are exceedingly unreactive; most reagents that attack them at all degrade them to the point where the results are no longer significant. Their structure therefore had to be established by independent syntheses. An attempt to synthesize the product that had been obtained with phenylmagnesium bromide by a Friedel and Crafts reaction was balked at the outset by the ease with which triphenyl propionyl chloride was converted into an indene derivative. Another attempt to synthesize it by the interaction of sodium triphenyl methane and α-chloro acetomesitylene in liquid ammonia was equally unsuccessful, the ketone merely exchanging one of its hydrogen atoms for sodium

$$(C_6H_5)_3CNa + ClCH_2COC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_3CH + ClCH{=}C(ONa)C_6H_2(CH_3)_3$$

The synthesis of the saturated ketone was, however, readily accomplished by taking advantage of the fact that when acetomesitylene is treated with a Grignard reagent it forms a halomagnesium enolate which reacts essentially like the metallic derivatives of acetoacetic ester.[3] Under proper conditions this enolate reacted with triphenylmethyl chloride to form the same substance that was obtained by the action of phenylmagnesium bromide an the unsaturated ketone



$$(C_6H_5)_2C{=}CHCOC_6H_2(CH_3)_3 + C_6H_5MgBr \longrightarrow$$
$$\underset{\text{I}}{} \quad (C_6H_5)_3CCH{=}\underset{\underset{\text{OMgBr}}{|}}{C}C_6H_2(CH_3)_3 \longrightarrow \underset{\text{II}}{(C_6H_5)_3CCH_2COC_6H_2(CH_3)_3}$$
$$(C_6H_5)_3CCl + CH_2{=}\underset{\underset{\text{OMgBr}}{|}}{C}C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_3CCH_2COC_6H_2(CH_3)_3 + MgClBr$$

Owing to the difficulty of preparing pure methyl diphenyl chloro methane this device could not be used for establishing the structure of the product obtained with methylmagnesium iodide, but equally conclusive evidence was secured in a different manner. By analogy with the reaction of phenylmagnesium bromide, methylmagnesium iodide would be expected to form methyl diphenyl propionyl mesitylene and this same ketone should be formed by the action of phenylmagnesium bromide on β-methyl benzalacetomesitylene. This was found to be the case.

$$\text{A.}\quad \underset{\text{I}}{(C_6H_5)_2C{=}CHCOC_6H_2(CH_3)_3} + CH_3MgI \longrightarrow$$
$$(C_6H_5)_2(CH_3)CCH{=}C(OMgI)C_6H_2(CH_3)_3 \longrightarrow \underset{\text{III}}{(C_6H_5)_2(CH_3)CCH_2COC_6H_2(CH_3)_3}$$

$$\text{B.}\quad \underset{\text{IV}}{(C_6H_5)(CH_3)C{=}CHCOC_6H_2(CH_3)_3} + C_6H_5MgBr \longrightarrow$$
$$(C_6H_5)_2(CH_3)CCH{=}C(OMgBr)\,C_6H_2(CH_3)_3 \longrightarrow \underset{\text{III}}{(C_6H_5)_2(CH_3)CCH_2COC_6H_2(CH_3)_3}$$

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(3) Kohler and Baltzly, THIS JOURNAL, 54, 4015 (1932).

These results show that, though difficult, it is not impossible to add Grignard reagents to β-phenyl benzalacetomesitylene and analogous compounds—the hydrocarbon residues as usual going into the beta position. The difference in the speed with which the several addition reactions occur is surprising. Thus, although the two reactions represented by A and B result in the formation of the same magnesium derivative, the first requires for completion at least three hours at the boiling point of benzene, while the second proceeds almost as fast as the reactants are brought together at the ordinary temperature. This great difference in rate appears to be due largely to a difference in the quality of the conjugated system, because methylmagnesium iodide can be substituted for phenylmagnesium bromide in the second reaction without materially altering its speed.

$$CH_3C(C_6H_5){=}CHCOC_6H_2(CH_3)_3 + CH_3MgI \longrightarrow$$
$$(CH_3)_2C(C_6H_5)CH{=}C(OMgI)C_6H_2(CH_3)_3 \longrightarrow (CH_3)_2C(C_6H_5)CH_2COC_6H_2(CH_3)_3$$

Experimental Part

β-Phenyl benzalacetomesitylene has been obtained heretofore by means of a series of reactions that are not well adapted for making larger quantities of the substance. We therefore devised a new method of preparation which is modeled after the best method for obtaining β-phenyl benzalacetophenone and which is indicated by the following series of compounds

$$\underset{A}{C_6H_5CH{=}CHCOC_6H_2(CH_3)_3} \longrightarrow \underset{B}{C_6H_5CHBrCHBrCOC_6H_2(CH_3)_3} \longrightarrow$$
$$\underset{C}{C_6H_5COCH_2COC_6H_2(CH_3)_3} \longrightarrow \underset{D}{(C_6H_5)_2COHCH_2COC_6H_2(CH_3)_3} \longrightarrow$$
$$\underset{I}{(C_6H_5)_2C{=}CHCOC_6H_2(CH_3)_3}$$

Benzalacetomesitylene, the first substance in the series, was originally prepared by the action of cinnamoyl chloride on mesitylene. It is much more easily obtained in quantity by the usual condensation of an aldehyde with a methyl ketone. Our procedure was as follows

To a solution of 62 g. of sodium hydroxide in 540 cc. of water, and 270 g. of alcohol was added, first 200 g. of acetomesitylene and then, gradually, with vigorous stirring, 146 g. of freshly distilled benzaldehyde. After stirring for six hours the mixture was cooled with ice and salt and inoculated, the stirring being continued to produce small crystals. The mixture crystallized rapidly and completely. The solid was washed with water until free from base and then with 25% alcohol to remove organic impurities. The yield of crude dry product was 290 g. or 94%. The crude product is sufficiently pure for the next step.

From the unsaturated ketone the dibromide (B) was obtained in the usual manner. In working with large quantities of material it is essential that the bromine be added slowly and with vigorous stirring, and also that it be not added in excess, otherwise some of it enters the mesitylene group and it is impossible to get bromine-free products in subsequent operations. From 290 g. of crude unsaturated ketone we obtained 357 g. of pure recrystallized product melting at 126–127°—a yield of 76%.

In a flask provided with a stirrer, a reflux condenser and a dropping funnel, 357 g. of the pure dibromide was mixed with 250 cc. of dry methyl alcohol. From the dropping funnel a solution of 39 g. of sodium in 380 cc. of dry methyl alcohol was added gradually while the flask was cooled with running water, the stirrer being started as soon as the mixture became sufficiently fluid. After all the methylate had been added, the mixture was boiled for three hours, then diluted with enough water to dissolve the sodium bromide and acidified with hydrochloric acid. The acidified solution was boiled for three hours, then cooled in ice water while it was stirred vigorously to prevent the formation of large lumps. It deposited a solid which after washing with water and with 50% alcohol yielded 219 g. of crude dry product. On recrystallization from methyl alcohol 20–30% of the material was left in the filtrates, the yield of pure product being 70–80%.

Anal. Calcd. for $C_{18}H_{81}O_2$: C, 81.2; H, 6.8. Found: C, 80.9; H, 6.8.

Benzoylacetomesitylene (C) is moderately soluble in all common organic solvents except petroleum ether in which it dissolves but sparingly. It crystallizes in colorless prisms and melts at 79°. A bromine titration by the Kurt Meyer method showed that like other aromatic diketones it is completely enolic. and in a quantitative examination with methylmagnesium iodide it reacted with two moles of reagent and liberated one mole of gas.

The diketone was converted into the β-hydroxy ketone (D) in the following manner. A solution of 50 g. of the substance in dry ether was added gradually to a similar solution of phenylmagnesium bromide. The mixture was boiled until the purple-red color which developed in the solution disappeared—usually five to six hours. At this stage the solution contained a dimagnesium compound which is stable but in order to isolate the carbinol, which readily loses water, it was necessary to proceed with great caution. The mixture was added slowly with efficient stirring to ice and hydrochloric acid, the ethereal layer washed with sodium carbonate, dried and allowed to evaporate spontaneously. It left a yellow oil which solidified when its solution in methyl alcohol was cooled in a freezing mixture. The solid was purified by recrystallization from methyl alcohol.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0. Found: C, 83.6; H, 7.2.

The carbinol is moderately soluble in ether, in benzene and in petroleum ether. It crystallizes in thick colorless plates and it melts at 75°.

β-Phenyl Benzalacetomesitylene, I.—From the carbinol the unsaturated ketone is readily obtained by warming it with aqueous hydrochloric acid but since it is easier to isolate and purify the ketone than the carbinol it is best to prepare it directly from the dimagnesium compound. This was accomplished by adding an equal volume of constant boiling hydrochloric acid to the ethereal layer obtained by decomposing the magnesium derivative, distilling off the ether, and warming the residue on a steam-bath for half an hour. The yellow oil solidified on cooling. The solid was recrystallized from methyl alcohol, from which it separated in thin plates melting at 104°. The yield was 82%.

β-Methyl Benzalacetomesitylene, IV.—By a slight modification of the method which has just been described it was also comparatively easy to prepare the methyl ketone which was needed for the structural work, the steps being represented as

$$C_6H_5COCH_2COC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)(CH_3)C(OH)CH_2COC_6H_2(CH_3)_3 \longrightarrow$$

$$(C_6H_5)(CH_3)C{=}CHCOC_6H_2(CH_3)_3$$

IV

The procedure was as follows. A solution of methylmagnesium iodide made from 2.3 g. of magnesium was added gradually to a solution of 25 g. of benzoyl acetomesitylene in 150 cc. of ether. The mixture, which had developed a purple color during the addition of the reagent, was boiled for seven hours, and then decomposed with iced acid in the usual manner. The ethereal layer, on evaporation, left a yellow oil which solidified when it was heated for half an hour with dilute hydrochloric acid. The solid was purified by recrystallization from petroleum ether from which it separated in large yellow prisms melting at 84°. The yield was 92.4%.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.4; H, 7.6. Found: C, 85.8; H, 7.6.

The unsaturated ketone is moderately soluble in the common organic solvents Its structure was established by ozonization, the ozonide yielding acetophenone, identified as m-nitro benzalacetophenone, and mesitylene carboxylic acid, which was identified by comparison with a specimen on hand.

Action of **Phenylmagnesium** Bromide on Phenyl Benzalacetomesitylene, **β,β,β-Triphenyl Propiomesitylene (II).**—The unsaturated ketone combines with phenylmagnesium bromide to form a red intermediate complex compound which is sparingly soluble in ether, and which regenerates the ketone when it is acidified. In order to carry the reaction beyond this preliminary stage it is necessary to use dilute solutions and to add the ketone at such a slow rate that the intermediate never crystallizes from the solution. Our best results were obtained as follows. A solution of **5** g. of the ketone in **125** cc. of dry ether was added during a period of three to four hours to a solution of the reagent which had been prepared from **1.6** g. of magnesium. The mixture was boiled for five hours more, or until the red color of the solution disappeared completely. After the usual manipulation, the mixture yielded a solid product which was recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{30}H_{28}O$: C, **89.1;** H, **6.7.** Found: C, **89.0;** H, **7.0.**

The saturated ketone is sparingly soluble in alcohol and ether. From glacial acetic acid it crystallizes in needles melting at 194–195°. The yield was only 60% but no other product was formed. By distilling the filtrates with steam and crystallizing the residue enough unsaturated ketone was recovered to account for all the material that had been used.

Structure of the Addition Product.—A solution of the bromomagnesium enolate of acetomesitylene was prepared by adding **16.2** g. of acetomesitylene to a solution of ethylmagnesium bromide made from **2.6** g. of magnesium and boiling the mixture for ten minutes. To this solution was added an ethereal solution of **28** g. of triphenylmethyl chloride. After a few minutes' boiling the mixture solidified. The solid, washed with water and recrystallized from glacial acetic acid, yielded **21.5** g. of the same product that had been obtained from β-phenyl benzalacetomesitylene.

Reaction with Methylmagnesium Iodide, **β,β-Diphenyl Butyrylmesitylene (III).**—After a number of fruitless attempts to carry out the reaction in ether, the following procedure was found to be effective. **A** solution of **5** g. of the ketone in **75** cc. of benzene was added in the course of half an hour to a boiling ethereal solution of methylmagnesium iodide prepared from **1.6** g. of magnesium. The resulting red solution was boiled for three hours and then decomposed in the usual manner. The benzene, on evaporation, left an oil, but when a solution of the oil in petroleum ether was cooled in a freezing mixture it deposited **3.6** g. of solid. Another gram of the same solid was obtained by distilling the filtrate with steam and treating this residue also with petroleum ether. The total yield, therefore, was **82%.**

Anal. Calcd. for $C_{25}H_{26}O$: C, **87.7;** H, **7.6.** Found: C, **87.4;** H, **7.8.**

The product is soluble in all common organic solvents including petroleum ether. It crystallizes in needles and it melts at **87°.** Its structure was established in the following manner. **A** solution of **5 g.** of 8-methyl benzalacetomesitylene in **75** cc of ether was added in the course of five minutes to a solution of phenylmagnesium bromide prepared from **2** g. of magnesium. Since the color of the red intermediate addition product disappeared rapidly, the mixture was decomposed with iced acid a few minutes after all of the ketone had been added. It yielded **4.0** g. of the same product which had been obtained by the action of methylmagnesium iodide on phenyl benzalacetomesitylene. The reaction was evidently incomplete, because the yield was only 62% and nearly a fourth of the unsaturated ketone was recovered, but the yield was diminished when the mixture was boiled for several hours before it was acidified.

Reaction with Ethylmagnesium Bromide, β,β-Diphenyl Valerylmesitylene C_2H_5C-$(C_6H_5)_2CH_2COC_6H_2(CH_3)_3$.—A solution of 6 g. of phenyl benzalacetomesitylene in 250 cc. of dry ether was added in the course of three hours to a solution of ethylmagnesium bromide prepared from 1.2 g. of magnesium. The color of the red intermediate compound was very persistent but it gradually faded to a light pink when the mixture was boiled for four hours. By decomposition with iced hydrochloric acid, and the usual manipulation of the ethereal layer, the mixture yielded a solid which separated from petroleum ether in needles and which melted at 106°.

Anal. Calcd. for $C_{26}H_{28}O$: C.87.6; H, 7.9. Found: C, 87.4; H, 7.7.

β-Methyl Benzalacetomesitylene and Methylmagnesium Iodide, $(C_6H_5)(CH_3)_2$-$CCH_2COC_6H_2(CH_3)_3$.—An ethereal solution of 5 g. of methyl benzalacetomesitylene was added in the course of a few minutes to an ethereal solution of methylmagnesium iodide which had been prepared from 1.8 g. of magnesium. The orange-colored solution soon began to deposit a colorless magnesium derivative. After ten minutes at the ordinary temperature it was decomposed with ice and acid in the usual manner. It yielded a solid which crystallized from acetic acid in colorless needles and which melted at 184–185°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85 8; H, 8.6. Found: C, 86.0; H, 8.8.

Summary

The former statement that β-phenyl benzalacetomesitylene does not add phenylmagnesium bromide is incorrect. Both β-phenyl and β-methyl benzalacetomesitylene add Grignard reagents, forming enolates of the corresponding saturated ketones.

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The Number of Stereoisomeric and Non-Stereoisomeric Alkines

BY DONALD D. COFFMAN

Since the number of structurally isomeric alkines[1] can be readily deduced from the number of structurally isomeric mono-substitution products of the paraffins,[2] an attempt has been made to calculate the number of stereoisomeric alkines.

Blair and Henze have advanced recursion formulas which[3] permit the calculation from their carbon content of the number of stereoisomeric and non-stereoisomeric primary, secondary and tertiary mono-substitution products of the paraffins. The use of these formulas depends upon the knowledge of the total number of stereoisomeric and non-stereoisomeric mono-substituted paraffins of every lower carbon content. By employing the published data of Blair and Henze, it is possible to calculate the number of stereoisomeric and non-stereoisomeric mono-substituted and

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(1) Coffman, and Blair with Henze, THIS JOURNAL, 55, 252 (1933).

(2) Henze and Blair, *ibid.*, 53, 3042–3046 (1931).

(3) Blair and Henze, *ibid.*, 54, 1098–1106 (1932).

di-substituted alkines of the formulas RC≡CH and RC≡CR′. The calculation depends upon the classification of the alkines into simple types whose number of stereoisomers may be estimated.

Mono-substituted **Alkines.**—The structural formulas of the mono-substituted alkines RC≡CH of N total carbon content may be formed by attaching to the residue —C≡CH each alkyl group R of $N-2$ carbon atoms. It is therefore apparent that the number of stereoisomeric mono-substituted alkines of N total carbon content formed in this way will equal the total number of stereoisomeric mono-substituted paraffins of all types containing $N-2$ carbon atoms. For these same reasons the number of non-stereoisomeric mono-substituted alkines of N total carbon content will equal the total number of non-stereoisomeric mono-substituted paraffins of all types containing $N-2$ carbon atoms. These values may be obtained from the tables of Blair and Henze.

Di-substituted **Alkines.**—The structural formulas of the di-substituted alkines RC≡CR′ of N total carbon content may be formed by attaching to the residue —C≡C— the alkyl groups R and R' (the sum of the carbon atoms in R and R' must always equal N—2). The total number of isomers that may be formed in this manner will be determined by the number of possibilities of combining with the residue —C≡C— complementary values of R and R . These combinations may be divisible into two types: (1) in which R and R' may be of[4] unequal carbon content, and *(2)* in which R and R' may be of equal content. As a matter of fact, type (2) is impossible for RC≡CR′ of an odd number of carbon atoms since $(N-2)/2$ must be an integer, greater than zero.

Type I.—When R and R' are of unequal carbon content, the number of possibilities of combining stereoisomeric and non-stereoisomeric values of R and R' with the residue —C≡C— may be represented by the expression $A_{s_i} \cdot A_{s_j} + A_{s_i} \cdot A_{n_j} + A_{n_i} \cdot A_{s_j}$ in which A, and A_{s_j} represent the total number of all types of stereoisomeric mono-substituted paraffins RX and R X each of carbon contents i and j, and in which A_{n_i} and An, represent the total number of all types of non-stereoisomeric mono-substituted paraffins RX and R'X each of carbon contents i and **j.** Here i and j are integers, distinct, and greater than zero, $i > j$, and $i + j = N-2$. By defining $T_i = A_{s_i} + A_{n_i}$ and $T_j = A_{s_j} + A_{n_j}$, substitution in and simplification of the above expression yields a formula representing the total number of stereoisomeric alkines RC≡CR′ of type 1

$$\Sigma(T_iT_j - A_{n_i}A_{n_j}) \qquad (\mathrm{I_s})$$

When N is even, the number of $T_i \cdot T_j - A_{n_i} \cdot A_{n_j}$ terms in the summation will be $(N-4)/2$; when N is odd, the number of terms will be $(N-3)/2$.

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(4) These types are analogous to those of the secondary mono-substitution products of the paraffins as classified by Blair and Henze.

The number of non-stereoisomeric alkines RC≡CR′ of type 1 will be equal to

$$\Sigma A_{n_i} . An, \qquad (I_n)$$

requiring $(N-4)/2$ terms when N is even, and $(N-3/2)$ terms when N is odd.

Type 11.—When R and R' are of equal carbon content, it is convenient to subdivide the isomers further into two groups: (a) in which R and R' are structurally and stereoisomerically identical, and (b) in which R and R′ are not identical.

Group (a).—The number of possibilities of combining identical stereoisomeric values of R and R' with the residue —C≡C— will equal the number of stereoisomers of this subdivision, or A_{s_i}. By the combination of identical non-stereoisomeric values of R and R′ with the residue —C≡C—, no stereoisomers can result.

Group (b).—When non-identical complementary values of R and R′, both stereoisomeric and non-stereoisomeric, are combined with the residue —C≡C—, the number of such possibilities may be represented by the expression $A_{s_i} . A_{n_i} + A_{s_i}(A, -1)/2$. The sum of the expressions in group (a) and group (b) gives a formula representing the total number of stereoisomers of type II.

$$A_{s_i}(2A_{n_i} + A_{s_i} + 1)/2 \qquad (II.)$$

in which i is an integer greater than zero, and $i = (N-2)/2$.

TABLE I

ISOMERIC ALKINES

Carbon content	RC≡CH Stereo	RC≡CH Non-stereo	RC≡CR′ Stereo	RC≡CR′ Non-stereo	RC≡CH and RC≡CR′ Total stereo	RC≡CH and RC≡CR′ Total Non-stereo	Total isomers
3	0	I	0	0	0	1	1
4	0	1	0	1	0	2	2
5	0	2	0	1	0	3	3
6	2	3	0	3	2	6	8
7	6	5	2	5	8	10	18
8	20	8	8	11	28	19	47
9	60	14	30	19	90	33	123
10	176	23	101	38	277	61	338
11	512	39	316	68	828	107	935
12	1,488	65	975	129	2,463	194	2,657
13	4,326	110	2,948	232	7,274	342	7,616
14	12,648	184	8,878	428	21,526	612	22,138
15	37,186	310	26,622	768	63,808	1,078	64,886
16	109,980	520	79,980	1,393	189,960	1,913	191,873
17	327,216	876	240,590	2,487	567,806	3,363	571,169
18	979,020	1,471	726,238	4,460	1,705,258	5,931	1,711,189
19	2,944,414	2,475	2,199,070	7,924	5,143,484	10,399	5,153,883
20	8,897,732	4,159	6,683,108	14,095	15,580,840	18,254	15,599,094
21	27,004,290	6,996	20,378,720	24,925	47,383,010	31,921	47,414,931
22	82,287,516	11,759	62,347,546	44,065	144,635,062	55,824	144,690,886

The number of possibilities of combining non-stereoisomeric values of R and R' (type II) with the residue —C≡C— may be represented by the expression $A_{n_i} + A_{n_i}(A_{n_i} - 1)/2$ which on simplification yields

$$A_{n_i}(A_{n_i} + 1)/2 \qquad (\mathrm{II_n})$$

representing the number of non-stereoisomeric alkines RC≡CR' of type II.

The finite formulas $\mathrm{I_s}$, $\mathrm{I_n}$, $\mathrm{II_s}$ and $\mathrm{II_n}$ permit the calculation of the number of stereoisomeric and non-stereoisomeric di-substituted alkines RC≡CR' of N total carbon content when the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of all types of $N - 3$ and every lower carbon content is known. In applying these formulas the values for the stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins, as calculated by Blair and Henze, have been employed. The table indicates the calculated number of stereoisomeric and non-stereoisomeric alkines containing from three to twenty-two carbon atoms inclusive.6

Summary

The number of stereoisomeric and non-stereoisomeric mono-substituted alkines RC≡CH of N total carbon content has been deduced from the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins.

The number of stereoisomeric and non-stereoisomeric di-substituted alkines RC≡CR' of N total carbon content has been calculated employing finite recursion formulas. The use of these formulas is dependent upon the knowledge of the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of $N - 3$ and every lower carbon content. The number of isomers so obtained agrees with the number required by theory through the decines as shown by writing the formulas and counting the stereoisomeric and non-stereoisomeric alkines RC≡CR'.

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(5) The number of stereoisomeric and non-stereoisomeric disubstituted alkines RC≡CR', as represented in the table, agrees exactly with the number obtained by writing and counting the structural formulas inclusive of the decines RC≡CR'.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Alpha Unsaturated Hydrocarbons[1]

BY CHARLES D. HURD[2] AND HARRY T. BOLLMAN[3]

To extend our knowledge of the pyrolysis of olefins beyond the C_5 members, these unsaturated hydrocarbons were chosen for study: diallyl, 4-methyl-1-pentene, allylcyclohexane and 4-phenyl-1-butene. All possess the general structure $R—CH_2CH=CH_2$, wherein R is a radical of low electron attraction. In contrast to propylene and isobutylene,[4] which required temperatures of 700° or above for extensive decomposition, these olefins decomposed considerably in the 425–500° range. Both types possess a $C\overset{\alpha}{—}C=C$ skeleton but the former has no $C\overset{\beta}{—}C\overset{\alpha}{—}C=C$ skeleton. This difference suggests that pyrolysis produces a rupture of the $C\overset{\beta}{—}C$ bond more readily than the $C\overset{\alpha}{—}C$.

Confirmation was found in the fact that propylene predominated throughout in the gases. The ethylene content was small, indicating an inconsiderable $C\overset{\alpha}{—}C$ scission. Saturated hydrocarbons and hydrogen comprised most of the remainder of the gas. Allene was sought for but not found.

In the lower boiling liquid products, materials were encountered which possessed slightly higher distillation ranges than the original hydrocarbon. They gave higher n_D values and, in the case of the liquid from diallyl, showed a different behavior toward tetranitromethane reagent. These facts suggest the presence of isomeric unsaturated hydrocarbons (such as 1,4- or 2,4-hexadiene from diallyl; 4-phenyl-2-butene from 4-phenyl-1-butene; etc.) or dehydrogenated compounds (such as 1,3,5-hexatriene from diallyl; phenylbutadiene or naphthalene from 4-phenyl-1-butene; etc.). Naphthalene was isolated in quantity from the phenylbutene liquids.

To compensate for the propylene found in the gas, much toluene (and some benzene) was formed from the phenylbutene. Similarly, cyclohexane, benzene and cyclohexene were indicated in the liquids from allylcyclohexane. Polymerization products were formed in every case, as shown by the high boiling material and tars which were encountered.

Mechanism.—The facts are best explained by assuming that these α-olefins undergo a preliminary scission into radicals at the allyl bond:

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(1) This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work was received from a research fund of the A. P. I. donated by the Universal Oil Products Co. This fund was administered by the Institute with the coöperation of the Central Petroleum Committee, National Research Council.

(2) Director, Project No. 18.

(3) American Petroleum Institute junior Research Fellow.

(4) Hurd, Spence and Meinert, This JOURNAL, 51, 3561 (1929); 62, 4978 (1930).

$R—C_3H_5 \longrightarrow R— + C_3H_5—$. These radicals acquire hydrogen atoms from some source, presumably largely from the original hydrocarbon, and escape as $RH + C_3H_6$. The dehydrogenated material may escape as $R'CH{=}CH—CH{=}CH_2$ or, in common with the original unsaturated hydrocarbon, it may undergo polymerization.

The formation of propylene without allene from diallyl resembles the analogous formation of aniline without allene from allylaniline[5] and of methane without allene from isobutylene.[6] A compound analogous to diallyl, namely, tetraphenylhexadiene, $(Ph_2C{=}CH—CH_2—)_2$, has been reported[7] to pyrolyze into α,α-diphenylpropylene and tar. The tar was regarded as polymerized diphenylallene but this position now becomes untenable.

A conclusion may be drawn from the present work regarding the pyrolysis of hydrocarbons in general, namely, that simple scission into two compounds should not be considered the primary effect even though each of the two products may be among the products of the reaction (as in the case of ethane + ethylene, or methane + propylene, from n-butane).

Experimental Part

Preparation of Hydrocarbons.—The compounds studied were synthesized by the general method:[8] $RMgX + BrCH_2CH{=}CH_2 \longrightarrow RCH_2CH{=}CH_2 + MgBr$. In the synthesis of diallyl it was found convenient to use much less ether than Cortese recommended and to add the allyl bromide slowly. The *diallyl* used boiled at 58–60'. For the *allylcyclohexane*, b p. 148–150°, these new constants were determined: d_4 = 20°/0.8160; 28.5°/0.8117; 41.5°/0.8010; n_D = 15°/1.4528; 25°/1 4483 The *dibromide of allylcyclohexane* gave these constants: b. p. 129–131 (11 mm.); n_D = 15°/1.5293, 20°/1 5271, 25°/1.5251. To synthesize *4-phenyl-1-butene*, benzylmagnesium chloride was used rather than the bromide. The hydrocarbon boiled at 175–178°; n_D^{20} 1.5090.

4-Methyl-1-pentene has not been made previously by this method. It was prepared from 24 g. of magnesium, 123 g. of isopropyl bromide in 150 cc. of dry ether, and 110 g. pf allyl bromide in 250 cc. of ether. It was converted[g] (in ether solution) into the dibromide and the latter dehalogenated with zinc and alcohol. The weight of olefin, b. p. 52.5–54.5°, was 33 g. Based on the allyl bromide, this represents a 43% yield.

Method of Heating.—Except for the manner of introducing the liquid hydrocarbons at a uniform rate into the unpacked Pyrex reaction tube, namely, by displacement with mercury, the method of heating and of collecting the products was very similar to that described for isobutylene.[10] The data from some representative experiments are summarized in Table I.

In several experiments with diallyl, the gases were passed through bromine in carbon tetrachloride. In a typical case, 21.5 g. of liquid, b. p. 139–140°, n_D^{20} 1.5206, was formed. These data characterized the liquid as 90% propylene bromide and 10% ethylene bromide There was about a gram of residue, 0.9 g. of which was butadiene tetrabromide, m. p. 114". Allene tetrabromide was not formed.

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(5) Carnahan and Hurd, THIS JOURNAL, 52, 4586 (1930).

(6) Hurd and Spence, *ibid* , 51, 3568 (1928); Hurd and Meinert, *ibid.*, 52, 4982 (1930).

(7) Wittig and Leo, *Ber.*, 63, 943 (1930).

(8) Diallyl, Cortese, THIS JOURNAL, 51, 2267 (1929); allylcyclohexane, Resseguier, *Bull. soc. chim.*, [4] 7, 431 (1910); 4-phenyl-1-butene, Lévy and Sfiras, Comfit. rend., 184, 1335 (1927).

(9) Boord and co-workers, THIS JOURNAL, 52, 3396 (1930); 54,754 (1932)

(10) Hurd and Spence, ibid., 51, 3563 (1929)

TABLE I

PYROLYSIS OF FOUR UNSATURATED HYDROCARBONS

Temp., °C.	Vol. tube, cc.	Time, min.	Liq. used, g.	Products cond. by ice, g.	CO_2 used as diluent, cc.[c]	Contact time, sec.	Decomposition, %	Gas formed, cc.	Gaseous products, per cent. by volume						
									C_2H_2	Sol. in 62% H_2SO_4	C_3H_6	C_2H_4	H_2	C_nH_{2n+2}	n
								Diallyl							
425	250	10	24.0	22.7	666	8	13	188	..	2.38	72.02	4.69	...	20.91	1.80
450	250	21	22.1	17.3	807	17	62	853	..	1.24	63.06	4.04	7.41	24.24	1.88
475	250	13	22.7	17.8	510	11	56	1308	3.25	5.29	63.65	4.01	4.01	19.78	1.84
500	520	8	22.5	16.1	594	13	66	2034	..	2.49	63.89	3.49	2.83	28.30	2.07
550	520	43	17.3	7.7	3909	52	91	4450	1.26	1.43	56.12	5.28	7.85	27.30	2.07
485	220[a]	15	21.9	16.6	2036	9	77	1517	0.57	2.28	61.92	3.63	9.33	22.26	1.55
650	17[b]	42	30.9	11.5	None	1.5	95	8698	..	0.60	48.60	9.90	10.40	30.50	1.49
								4-Methyl-1-pentene							
600	250	50	28	7.9	None	31.4	73	4830	..	2.6	27.2	11.4	6.1	52.6	1.4
625	17[b]	108	23	7.1	None	5.5	87	8790	1.6	4.6	44.0	9.6	9.5	33.6	1.7
650	17[b]	101	25	6.2	None	4.6	95	10840	1.6	5.7	38.6	9.8	8.6	35.6	1.6
675	17[b]	74	28.8	5.9	None	2.8	96	12745	1.6	3.9	42.2	13.7	9.2	29.3	1.4
								Allylcyclohexane							
500	17[b]	42	27.6	25.1	None	3.0	25	..	..	..	...	...	..	...	..
550	17[b]	105	38.0	17.0	None	5.2	75	6110	0.5	1.7	36.3	16.9	7.3	37.4	1.9
600	17[b]	89	42.3	18.4	None	3.7	85	9548	0.4	2.7	38.2	21.0	11.0	26.7	1.5
650	17[b]	57	36.5	14.0	None	2.6	90	12320	..	3.2	34.2	21.3	10.9	30.4	1.4
								4-Phenyl-1-butene							
500	250	26	43.1	41.8	3910	12	27.5	610	..	3.5	74.6	4.7	7.6	9.6	2.3
500	250	76	46.9	44.4	5150	31	50	1260	..	1.1	59.7	10.6	10.5	18.1	2.0
550	250	57	49.7	43.3	1750	28	73	2530	..	1.2	46.8	10.0	15.9	26.1	1.7
600	250	13	28.2	22.9	482	12	88	2290	..	..	44.2	10.1	22.0	23.7	1.7
700	23	38	28.2	23.0	2770	2.3	77	2223	..	1.1	36.5	17.0	18.4	27.0	1.3

[a] Magnesium turnings in the tube about half filling the tube. [b] Quartz tube of small diameter used; Pyrex used elsewhere. [c] In experiments in which carbon dioxide was used, a steady flow of the gas was maintained throughout the experiment. This item was considered in calculating the contact time: Contact time = (vol. tube × time in sec. × 273)/$T°$ Abs. (((22400 × wt.)/mol. wt.) + vol. CO_2).

Some gas from a 500° run was cooled by liquid air. The condensate was distilled, the first fraction including everything from −190 to −80° (200 cc.) and the second from −80° to room temperature (300 cc.). Propylene, ethylene, methane and ethane (n in C_nH_{2n+2} was 1.23) were found in the first fraction. The last fraction contained much more propylene and a little ethane (n = 2.04). Propane and butane were not indicated.

A trace of butadiene (but no allene) was also found by brominating the gases from 4-methyl-1-pentene or allylcyclohexane. The saturated hydrocarbons from 4-methyl-1-pentene were methane and ethane. No liquid (propane or butane) condensed from it at −80°.

Liquid Products.—The extent of the decomposition was determined by distilling off the unused hydrocarbon from the condensed liquids. Obviously this method lacked the precision which was possible in work with gaseous hydrocarbons. From a 500° run with diallyl, the 16.1 g. of liquid gave these fractions: (°C., g, n^{22}_D) 58–60, 4.4, 1.406; 60–65, 3.7, 1.414; 65–75, 2.7, 1.440; above 75, 1.2, 1.465; and 4.2 g. of residue. In another run (485°), 8.97 g. in a 58–67" fraction was mixed with aniline and refractionated: (b. p., n^{20}_D) 58–60, 1.401; 60–63, 1.416; 63–69, 1.423. The 58–60" fraction was almost pure diallyl. A little of it, added to a mixture of 4 cc. of an ether solution of tetranitromethane and 2–3 drops of pyridine, caused no immediate coloration but in fifteen minutes a yellow-green color developed.[11] In contrast, the other fractions produced an almost immediate brown coloration. This may point to a conjugated hexadiene.

The high boiling residue from diallyl gave a solid, m. p. 47°, on bromination. Its bromine content was 66.3% and its molecular weight 476. This would be satisfactory for $C_{12}H_{20}Br_4$, $C_{12}H_{18}Br_4$ or $C_{12}H_{16}Br_4$.[12] The liquid and gaseous products were not markedly affected by the presence of magnesium[13] in the reaction tube.

Distillation of the liquids from allylcyclohexane gave volatile hydrocarbons (b. p. 70–145°), then recovered allylcyclohexane (145–150°), finally a tarry residue which was 4–5 times heavier than the volatile portion. The latter contained[14] aromatics, cycloalkanes and lesser amounts of cycloalkenes. The refractive index (20°) of the 78–85" fraction was 1.463, suggesting about equal parts of benzene and cyclohexene.

Fractionation of the liquids from the 550° run with 4-phenyl-1-butene gave 9.7 g. of benzene and toluene; 6 g. between 115–170°; 6.7 g., 170–178° (n^{20}_D 1.5225); 5 g., 178–185° (n^{20}_D 1.5268); 19.2 g. of residue about half of which was naphthalene. Some stilbene was also isolated from the residue. The 170–178° fraction contained the phenylbutene, but its high refractive index denoted a contaminant.

Summary

The pyrolysis of diallyl, 4-methyl-1-pentene, allylcyclohexane and 4-phenyl-1-butene was studied. All of these gave a predominating quantity of propylene as a gaseous product and none gave any allene. Liquid products were formed which pointed to isomerization, dehydrogenation and polymerization processes. A mechanism for these observations is outlined which also incorporates facts of other varied experiments on pyrolysis.

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[11] Werner, *Ber.*, 42, 4324 (1909), observed a yellow coloration with amylene.

[12] Compare Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913). for diallyl polymers obtained by heating diallyl for ten hours at 250°.

[13] For its effect on the dry distillation of rubber, which also contains a —C=C—C—C—C=C— skeleton, see Midgley and Henne, THIS JOURNAL, **51**, 1285 (1929).

[14] The method of Egloff and Morrell [*Ind. Eng. Chem.*, **18**, 354 (1926)] was used.

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

The Grignard Reaction in the Synthesis of Ketones. I. A New Method of Preparing Desoxybenzoins

BY SANFORD S. JENKINS

In order to facilitate certain studies, some of which have been published,[1a,b] dealing with desoxybenzoins a general method of synthesizing this interesting class of ketones was sought.

The object of this report is to describe a method that is more generally applicable than the usual ones and which appears to be entirely reliable in its indication of structure. Briefly, the method, which is an adaptation with certain improvements of that of Béis[2] for preparing aliphatic ketones, consists in condensing primary benzamides with benzylmagnesium halides. In order to obtain the maximum yields, however, there are two conditions to be observed: three to four equivalents of the halide to one of the amide must be used and long heating of the reactants is necessary.

In this manner benzyl phenyl, benzyl *m*-chlorophenyl, benzyl p-methoxyphenyl, o-chlorobenzyl p-methoxyphenyl and *p*-chlorobenzyl p-methoxyphenyl ketones were obtained in satisfactory yields.

Although rearrangements are known to take place when benzylmagnesium halides are condensed with certain substances,[3] no evidence of any abnormal product was obtained in this work. Where possible the products were compared directly with the desoxy ketones obtained in the reduction of the corresponding benzoins but since most of the latter compounds were either not available or have not been described, this procedure was supplemented by the Beckmann rearrangement of the ketoximes.[4] The structures of the resulting anilides were then established by comparison with authentic samples. When prepared according to the directions given below the oximes are all of the anti-benzyl type.

Experimental

Preparation of Ketones

Apparatus and Method.—A 500-cc. three-necked, round-bottomed flask is fitted with a mechanical stirring apparatus, a dropping funnel, and a condenser to which is attached a drying tube. A very satisfactory heater may be made by inserting an electric bulb in the apex of an inverted cone of asbestos paper the base of which is placed under the flask. When mounted on a single ringstand the apparatus is compact and convenient.

After placing the required amount of thin, bright magnesium turnings and a small crystal of iodine in the flask and connecting the various parts, the apparatus is swept out with dry hydrogen. A solution of the benzyl halide in 100 to 125 cc. of ether is

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(1) (a) Jenkins. THIS JOURNAL, 53, 3115 (1931); (b) *ibid.*, 54, 1155 (1932).

(2) Béis, *Compt. rend.*, 137, 575 (1903).

(3) Austin and Johnson, THIS JOURNAL, 54, 647 (1932).

(4) Günther, *Ann.*, 252, 68 (1889).

PREPARATIONAL DATA AND CONSTANTS OF KETONES WITH MOLECULAR WEIGHTS AND ANALYSES

Amide	Grignard reagent	Letter	Ketone	Yield, %	M. P., °C. (corr.)	Mol. wt. (Rast) Calcd	Found	Formula	Chlorine, % (Parr bomb) Calcd.	Found
$C_6H_5CONH_2$	$C_6H_5CH_2MgCl$	A	$C_6H_5COCH_2C_6H_5$	77	57	...	...	......	...	...
m-$ClC_6H_4CONH_2$	$C_6H_5CH_2MgCl$	B	*m*-$ClC_6H_4COCH_2C_6H_5$	72	62	230.5	226	$C_{14}H_{11}ClO$	15.37	15.58
p-$CH_3OC_6H_4CONH_2$	$C_6H_5CH_2MgCl$	C	*p*-$CH_3OC_6H_4COCH_2C_6H_5$	74	77	226	228	......	...	...
p-$CH_3OC_6H_4CONH_2$	*o*-$ClC_4H_5CH_2MgBr$	D[5]	*p*-$CH_3OC_6H_4COCH_2C_6H_4Cl$-*o*	55	97.5	260.5	247	$C_{15}H_{13}ClO_2$	13.60	13.72
p-$CH_3OC_6H_4CONH_2$	*p*-$ClC_6H_4CH_2MgBr$	E	*p*-$CH_3OC_6H_4COCH_2C_6H_4Cl$-*p*	66	137.5	260.5	266	$C_{15}H_{13}ClO_2$	13.60	13.81

The reactants were employed in the ratio of 0.050 mole of amide to 0.20 mole of Grignard reagent and were heated for forty to forty-eight hours. Ketones **A,** B, and C were obtained as white plates, D as white cubes and E as white diamond-shaped plates.

The yields are based on the amides and represent material that was crystallized once from alcohol. Ketone B is soluble in ether and benzene, fairly soluble in 80% alcohol and may be conveniently crystallized from ligroin (Skelly Solve "C"). E is sparingly soluble in ether and alcohol and is best purified by crystallization from benzene-petroleum ether solution.

The amides were obtained in the usual manner from the corresponding acids. "Baker's C. P. Analysed" benzyl chloride and Eastman best grade of o- and *p*-chlorobenzyl bromides were used in this work.

Ketone A was found to be authentic by comparison with desoxybenzoin obtained in the reduction of benzoin. Ketone C proved to be identical with one of the reduction products of benzanisoin.[1b]

The molecular weights were obtained by means of the Rast method using borneol instead of camphor.

TABLE II

YIELDS, CONSTANTS AND ANALYTICAL DATA OF OXIMES AND ANILIDES

From ketone	Phenyl ketoxime. *Anti*	Yield, %	M. p., °C (corr.)	Formula	Chlorine, % (Parr bomb) Calcd.	Found	Anilide	Yield. %	M. p., °C. (corr.)	Formula	Chlorine, % (Parr bomb) Calcd.	Found
A	Benzyl-	90	98				Phenylacet-	60	117.5			
B	Benzyl-m-chloro-	92	120	$C_{14}H_{12}NClO$	14.47	14.41	Phenylacet-*m*-chloro-	65	95	$C_{14}H_{12}NClO$	14.47	14.57
C	Benzyl-*p*-methoxy-	95	118.5				Phenylacet-*p*-methoxy-	60	124			
D[5]	o-Chlorobenzyl-p-methoxy	93	99	$C_{15}H_{14}NClO_2$	12.86	12.93	*o*-Chlorophenylacet-*p*-methoxy[5]	60	166	$C_{15}H_{14}NClO_2$	12.86	12.92
E	*p*-Chlorobenzyl-*p*-methoxy	88	138.5	$C_{15}H_{14}NClO_2$	12.86	12.91	*p*-Chlorophenylacet-*p*-methoxy-	60	184	$C_{15}H_{14}NClO_2$	12.86	13.07

The oximes were all obtained as white needles. Anilides **A** and C crystallized as white plates, B and D as white needles while E consisted of white leaflets.

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(5) Buck and Ide, THIS JOURNAL, 53, 1536 (1931).

placed in the dropping funnel and a small portion (10–15 cc.) added to the magnesium. The flask is now heated until the reaction is under way, after which the heat is cut off and the stirrer started. The solution is added at such a rate that gentle refluxing of the ether is maintained. After the addition the stirring is continued until the solution cools. The dropping funnel is now replaced by a ctak and by means of a long-handled spatula the dry, finely-powdered amide is added in portions, the rate of addition being determined by the vigor of the reaction. The heat is now turned on and the solution allowed to reflux with occasional stirring for the required time.

The complexes were decomposed by pouring the solutions into 200 g. of a slush of ice and water containing 20 g. of sulfuric acid. After standing at room temperature for an hour the ether was separated. The water layer was heated on the hot-plate for half an hour, cooled and extracted with ether. In this way an additional portion of ketone was obtained. The ether extracts were then combined and steam distilled. On cooling the yellow residue solidified and was crystallized from alcohol.

Ketones C, D and E, not being very soluble in ether, usually separated in part when the complexes were hydrolyzed.

Preparation of **Oximes.**—The oximes were prepared by mixing 2.00 g. each of ketone and hydrovylamine hydrochloride, 3.20 g. of potassium acetate and 40 cc. of alcohol. After standing overnight at room temperature the mixture was heated on the water-bath under reflux for three hours. Hot water was then added until a clear solution was obtained and a faint opalescence appeared. The solution was then set aside in a cool place and after several hours the crystals were filtered. Further crops were obtained by adding cold water to the filtrates.

The oximes of ketones C and E were also prepared by using 20 cc. of pyridine instead of the alcohol and potassium acetate, with identical results.

Preparation of Anilides

1. By Rearrangement of the **Oximes.**—To 1.00 g. of oxime dissolved in 30 cc. of absolute ether about 1.50 g. of powdered phosphorus pentachloride was added portionwise. The solution was shaken and kept cold during the addition. After standing at room temperature for half an hour the mixture was poured into 100 cc. of cold water and the ether driven off by means of a stream of air. The crude anilide was then separated and washed with water.

2. By Synthesis from the Acids or Acid Chlorides **and** the Corresponding **Anilines.**—(a) Anilides A, B and C were prepared in the Schotten–Baumann manner by mixing phenylacetyl chloride and the corresponding anilines.

(b) Anilides D and E were obtained from o- and p-chlorophenylacetic acids[6] and *p*-anisidine by heating the mixture in an oil-bath at 180–200° for two hours

The anilides as obtained by either method (1 or 2) were recrystallized from dilute alcohol until pure. Their identity was established by their mixed melting points and crystalline structures.

Acknowledgments

I wish to thank Prof. E. Emmet Reid for his interest and many valuable suggestions in this work, Messrs. J. R. Meadow and E. M. Richardson for making the molecular weight determinations and Mr. Richardson for assistance in the analyses.

Summary

A new method of synthesizing desoxybenzoins which appears to be of wide application has been described.

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(6) Mehner, *J. prakt. Chem.*, 62, 554 (1900).

From the appropriate primary benzamides and benzylmagnesium halides benzyl phenyl, benzyl m-chlorophenyl, benzyl p-methoxyphenyl, *o*-chlorobenzyl *p*-methoxyphenyl and *p*-chlorobenzyl p-methoxyphenyl ketones have been obtained in satisfactory yields.

No evidence of rearrangements has been obtained in this type of Grignard reaction.

Six new compounds were prepared and characterized.

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Stereochemistry of Diphenyls. XXVII.[1] Comparison of the Racemization of 2,2'-Difluoro-6,6'-dicarboxydiphenyl and 2,2'-Dimethoxy-6,6'-dicarboxydiphenyl

BY W. M. STANLEY, EDWARD MCMAHON[2] AND ROGER ADAMS

The methoxyl group has been shown in previous researches to have a smaller interference effect when substituted in the 2,2',6,6' positions than had at first been predicted. It was found impossible to resolve 2,2'-difluoro-6,6'-dimethoxy-3,3'-dicarboxydiphenyl[3] and the active 2-nitro-&carboxy-2'-methoxydiphenyl was very readily racemized.[4] The relative interference value of the methoxyl was thus revised from 1.56, as at first estimated, to 1.45. The latter value would conform to all the facts thus far assembled in connection with various hydroxylated and methoxylated diphenyls; the interconversion of the cis to the trans isomers of di-(3-bromo-2,4,6-trimethy1phenyl)2-5-dihydroxybenzoqinone[6] (interference on each side 0.135 Å.), the non-existence of two isomers in di-(2,4-dimethylphenyl)-2,5-dihydroxybenzoquinone[6] (interference on each side, —0.265 Å.) and in 2,2'6,6'-tetramethoxy-3,3'-dicarboxydiphenyl (interference on each side, 0.00 Å.).[7]

A more direct comparison of the methoxyl group and fluorine atom has now been made by the study of 2,2'-difluoro-6,6'-dicarboxydiphenyl (VI) and 2,2'-dimethoxy-6,6'-dicarboxydiphenyl. The two diastereoisomeric salts of each compound were isolated and from these the two active acids of each of the two diphenyls.

The active 2,2'-difluoro-6,6'-dicarboxydiphenyl was completely race-

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(1) For paper XXVI see Yuan and Adams, THIS JOURNAL, 54,4434 (1932).

(2) The experimental work on the fluorine derivatives was done by W. M. Stanley; that on the dimethoxy derivatives by Edward McMahon and was presented by him in a thesis for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

(3) Becker and Adams, THIS JOURNAL, 54, 2973 (1932).

(4) Stoughton and Adams, *ibid.*, 54, 4426 (1932).

(5) Shildneck and Adams, *ibid.*, 53, 343, 5303 (1931).

(6) Unpublished results of G. C. Finger.

(7) Unpublished results of M. C. Cupery.

mized when heated on a steam cone for eight minutes in 0.1 *N* sodium hydroxide and a marked diminution in rotation occurred when allowed to stand for one week at 2b° in 0.1 N sodium hydroxide. Complete racemization occurred in boiling alcohol in about two hours and in boiling acetic anhydride in ten minutes, and partial racemization was caused by boiling in glacial acetic acid for five minutes and by standing for one week at 25° in absolute ethyl alcohol containing 40% hydrochloric acid.

On the other hand, the active 2,2′-dimethoxy-6,6′-dicarboxydiphenyl racemized much more slowly, giving the following half-life periods: in boiling 0.1 *N* sodium hydroxide, seven hours and fifty minutes; in boiling sodium ethylate, eleven hours; in boiling glacial acetic acid, seventy-eight minutes; and in boiling alcohol about sixty hours.

The fluorine therefore is a considerably smaller interfering group than the methoxyl. On the basis of calculated values previously used, the interference in the 2,2′-difluoro would be 0.05 Å.; in the 2,2′-dimethoxy, 0.11 Å. on each side of the molecule if the value of 1.45 Å. for the methoxyl is adopted.

The discrepancy between the racemization rates of active 2,2′-dimethoxy-6,6′-dicarboxydiphenyl and of active 2-nitro-6-carboxy-2′-methoxydiphenyl[4] corresponds to the observed fact that for the same interference value, the rate of racemization of a 2,2′,6-trisubstituted compound is more rapid than that of a 2,2′,6,6′-tetrasubstituted compound.[1,4]

The active esters and amides of 2,2′-dimethoxy-6,6′-dicarboxydiphenyl were prepared and their rates of racemization determined. In glacial acetic acid, the half-life period values of the acid, ester and amide were seventy-eight, eighty-eight, and two hundred and forty minutes, respectively. The atom or group combined to the atom which is attached to the ring thus plays an appreciable part in the interference value of the whole group. A comparison is now being made of various esters and substituted amides of 2,2′-dimethoxy-6,6′-dicarboxydiphenyl to determine the relative effects of these groups.

Experimental

The difluoro acids was prepared from 1-nitro-2-iodo-3-carboxybenzene (III) by a series of reactions of which the stages are shown by the accompanying formulas.

Certain steps in this procedure are of particular interest. Kenner reported that acid reducing agents could not be used on (I) on account of the activity of the iodine atom. Nevertheless, it was found that the reduction could be accomplished by the action of stannous chloride and hydrochloric acid either with or without a little alcohol. The amino group could not be replaced by fluorine using the usual procedure through treatment of the diazonium chloride or diazonium fluoride with hydrofluoric or hydro-

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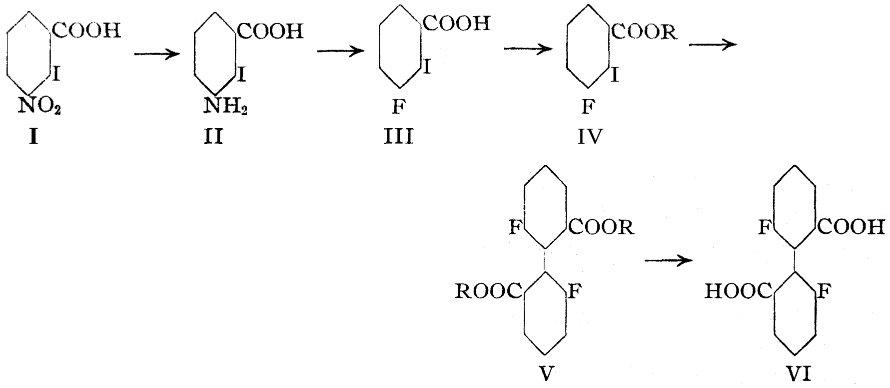
(8) Kenner and Turner [*Chem. & Ind.*, **46**, **218** (1927)] mentioned their intention of preparing 2,2′-difluoro-6,6′-dicarboxydiphenyl but as no description has appeared to date, it has been assumed that this particular research has been abandoned. See also Stanley and Adams, THIS JOURNAL, **52**, 1200 (1930).



borofluoric acid. Only by diazotization of the amino acid in 48% hydrofluoric acid and by then allowing the diazonium fluoride to stand for a considerable time at room temperature was the fluorine introduced.

1-Methoxy-2-nitro-3-carboxybenzene.—In a 3-liter three-necked flask, equipped with a stirrer and a reflux condenser, were placed 50 g. of 1-methyl-2-nitro-3-methoxybenzene and a solution of 160 g. of potassium permanganate in 2 liters of water. The mixture was refluxed, with stirring, for twelve hours. The manganese dioxide was removed by filtration and the filtrate concentrated to about 500 cc. The unoxidized material steam distilled during this process. Upon cooling and acidifying with 10% sulfuric acid 1-methoxy-2-nitro-3-carboxybenzene precipitated and was purified from 400 cc. of 95% alcohol. The yield was 26 g. (58%) of a product melting at 256–257° (corr.). Rieche[10] reports a m. p. of 251°.

1-Methoxy-2-amino-3-carboxybenzene.—A solution of 4 g. of the nitro acid in 100 cc. of hot 95% alcohol was reduced with 0.2 g. of platinum oxide and hydrogen at 2.5 atm. pressure in five minutes. A total of twenty-five such reductions was made, six to a single sample of catalyst. The alcoholic solution of all the 1-methoxy-2-amino-3-carboxybenzene thus obtained was filtered from the platinum and the alcohol distilled until the volume of the residual solution was about 600 cc. Upon cooling, 66 g. of tan-colored amino acid separated. Recrystallization from 95% alcohol raised the melting point to 171–172° (corr.). The mother liquor was evaporated to 300 cc. and cooled and a second crop of crystals obtained. The total yield was 71.5 g. (84%). Pschorr[11] reports m. p. 169–170°.

1-Methoxy-2-iodo-3-carboxybenzene.—To an ice-cold suspension of 60 g. of 1-methoxy-2-amino-3-carboxybenzene in 500 cc. of water containing 51 cc. of concentrated sulfuric acid was added, with stirring, a solution of 24.8 g. of sodium nitrite in 60 cc. of water. Stirring was continued in the cold for thirty minutes and the solution was then added, with stirring, to a boiling solution of 60 g. of potassium iodide in 200 cc. of water in a 3-liter three-necked flask equipped with a reflux condenser and a mechanical stirrer. The mixture was refluxed with stirring for thirty minutes while the evolution of nitrogen was vigorous and then allowed to cool (stirring continued) to room temperature. The product separated and was crystallized from 95% alcohol. The yield was 68 g. (68%) of a product melting at 148–149° (corr.). Kenner and Turner[9] report a melting point of 150–151°.

1-Methoxy-2-iodo-3-carbomethoxybenzene.—The acid was esterified with absolute

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[9] Kenner and Turner, J. *Chem Soc.*, 2340 (1928).

[10] Rieche, *Ber.*, 22,2352 (1889).

[11] Pschorr, Ann., 391, 27 (1912).

methanol containing a little concentrated sulfuric acid. The yield was 44.5 g. (96%). Upon recrystallization from 95% alcohol, white crystals melting at 56–57° were formed. (Kenner and Turners report a melting point of 57°.) The ester was used without recrystallization for the preparation of 2,2′-dimethoxy-6,6′-dicarbomethoxydiphenyl.

2,2′-Dimethoxy-6,6′-dicarbomethoxydiphenyl.—By heating 5 g. of 1-methoxy-2-iodo-3-carbomethoxybenzene and 10 g. of copper powder in a metal bath at 205–215° for one hour, extracting with boiling benzene and ether and evaporating, the product was obtained; yield, 16 g. from seven runs. It was purified by crystallization from benzene, m. p. 136–137° (corr.).

2,2′-Dimethoxy-6,6′-dicarboxydiphenyl.—The acid was obtained by the action of alcoholic potassium hydroxide on the ester. It was recrystallized from 95% alcohol. The yield was 12.3 g. (90%) of product melting at 293–294°. Kenner and Turner[8] report a melting point of 288–290 .

Resolution of 2,2′-Dimethoxy-6,6′-dicarboxydiphenyl

Monobrucine Salt.—To a hot solution of 1.305 g. of anhydrous brucine in 30 cc. of dry ethyl acetate was added a hot solution of 0.500 g. of 2,2′-dimethoxy-6,6′-dicarboxydiphenyl in 25 cc. of absolute methyl alcohol. Upon cooling for five hours a crop of fine white crystals weighing 0.96 g. separated. After recrystallization from absolute methyl alcohol the salt melted at 198–199° (corr.).

Rotation. 0.2000 g. made up to 20 cc. in chloroform at 20° gave α, +0.235°; 1 = 2; $[\alpha]^{20}_{D}$ +11.7°. Recrystallization from absolute methyl alcohol did not raise the melting point or change the rotation.

Kenner and Turner report the preparation of this compound and give a melting point of 268° but do not report its rotation.

Anal. Calcd. for $C_{39}H_{40}O_{10}N_2$: N, 4.02. Found: N, 4 02.

The remaining material which separated upon further evaporation of the solvent was found to be a mixture of the salt with unchanged brucine.

Diquinine Salt.—To a hot solution of 12.88 g. of anhydrous quinine in 80 cc. of absolute methyl alcohol was added a hot solution of 6 g. of 2,2′-dimethoxy-6,6′-dicarboxydiphenyl in 170 cc. of absolute methyl alcohol. Upon evaporation *in vacuo* at room temperature a dry residue was obtained which was heated to boiling with 200 cc. of dry acetone. Upon cooling, 9.79 g. of white crystals separated. After recrystallization from dry acetone, the salt melted at 178–179° (corr.).

Rotation. 0.2045 g. made up to 20 cc. in chloroform at 20° gave α, +2.27°; l = 2; $[\alpha]^{20}_{D}$ +111.0°. The salt, upon recrystallization from dry acetone, was not changed in melting point or rotation. Kenner and Turner[8] report a melting point of 172–173° and an $[\alpha]_D$ in chloroform of +126°.

Anal. Calcd. for $C_{56}H_{62}O_{10}N_4$: N, 5.90. Found: N, 5.80.

The mother liquor from the first crop of crystals was evaporated to 50 cc. by bubbling nitrogen through the solution. Upon cooling, 0.30 g. of salt separated. This was removed by filtration. The mother liquor was evaporated to dryness. The residue consisted of a resin which, when the last traces of solvent were removed, formed a white powder. The salt could be dissolved in acetone or ethyl acetate and precipitated as a white, flocculent mass by addition of petroleum ether (b. p. 20–40°). Upon filtration, however, this solid turned to a gummy mass which reverted to a white powder when all traces of the solvent were removed. The salt melted at 98–100° (corr.). The weight of salt thus obtained was 8.5 g.

Rotation. 0.1550 g. made up to 20 cc. in chloroform at 20° gave α_D −0.93°; l = 2; $[\alpha]^{20}_{D}$ −60°.

Anal. Calcd. for $C_{56}H_{62}O_{10}N_4$: N, 5.90. Found: N, 5.93.

Kenner and Turner[8] report that the more soluble salt melts at about 60° with decomposition and has an $[\alpha]_D$ in chloroform of −68°.

l-2,2'-Dimethoxy-6,6'-dicarboxydiphenyl.—A mixture of 3 g. of the less soluble salt and 40 cc. of 5% sodium hydroxide solution was ground in a mortar. This mixture was extracted with four 15-cc. portions of cold chloroform. The alkaline solution was then acidified with 6 N hydrochloric acid. The 1-acid precipitated as a white spongy mass which was filtered and dried. After drying, the compound was crystalline and melted at 291–292°.

Rotation. 0.0766 g. made up to 20 cc. in dry acetone at 20° gave α_D −0.88°; 1 = 2; $[\alpha]^{20}_D$ −114.9'.

Kenner and Turner[9] report a melting point of 294–295° and an [a], −115°.

The active acid was recrystallized from boiling chloroform, but apparently racemized somewhat during the procedure.

Rotation. 0.0785 g. made up to 20 cc. in dry acetone at 20' gave α_D −0.70°; 1 = 2; $[\alpha]^{20}_D$ −89.5'.

If the l-acid was dissolved in dry acetone and excess petroleum ether (b. p. 20–40°) was added, feathery crystals separated after standing in the cold for two hours. The melting point and rotation were unchanged by this treatment.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.64. Found: C, 63.7; H, 4.57.

d-2,2'-Dimethoxy-6,6'-dicarboxydiphenyl.—Three grams of the more soluble salt was decomposed by the procedure used for the less soluble salt. The d-acid obtained in this way melted at 291–292''.

Rotation. 0.0737 g. made up to 20 cc. in dry acetone at 20° gave a,, +0.80°; l = 2; $[\alpha]^{20}_D$ +108.5°.

The d-acid was recrystallized from boiling chloroform. Partial racemization took place.

Rotation. 0.0717 g. made up to 20 cc. in dry acetone at 20° gave α_D +0.62°; *1* = 2; $[\alpha]^{20}_D$ +86.5°.

The d-acid was then purified by dissolving in dry acetone and adding excess petroleum ether. The product had the same melting point and rotation.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.64. Found: C, 63.61; H, 4.77.

Racemization Experiments.—Only a few of the readings taken during the racemization experiments are given. Many more were recorded and from all of them the half-life periods were calculated.

In Sodium Hydroxide

Rotation. 0.0967 g. made up to 20 cc. in 0.1 N sodium hydroxide at 20° gave α_D −2.60'; l = 2; $[\alpha]^{20}_D$ −269°. After refluxing for fifty-five minutes the rotation was −256°; after eight hours, −137.5'; after twenty-three hours. −16.6°; after twenty-six hours, −10.3°; and after twenty-nine hours the rotation was zero. The half-life period was seven hours and fifty minutes.

In Sodium Ethylate

A solution of sodium ethylate was prepared by dissolving 0.50 g. of sodium in 100 cc. of absolute alcohol.

Rotation. 0.0678 *g.* of 1-acid made up to 20 cc. in sodium ethylate solution at 20° gave α_D −0.83°; 1 = 2; $[\alpha]^{20}_D$ −121.8'. After refluxing for two hours the rotation was −108'; after nine hours and thirty minutes, −67.8'; after twenty-three hours and thirty minutes, −36.9'; and after forty-four hours and thirty minutes, −3.9'. The half-life period was eleven hours.

In Ethanol

Rotation. 0.0880 g. made up to 20 cc. in 95% alcohol at 20° gave α −1.19°; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ −135.5°. After refluxing for forty-five minutes the rotation was −133°; after eight hours and twenty-five minutes, −125°; after twenty-nine hours and thirty minutes, −99°. The half-life period was sixty-one hours and thirty minutes.

In Glacial Acetic Acid

Rotation. 0.0670 g. made up to 20 cc. in glacial acetic acid at 20° gave α_{D} −1.13°; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ −168.5°. After refluxing for two hours and thirty minutes the rotation was −49.2°; after four hours, −20.9°; after five hours and forty-five minutes, −5.5°; and after seven hours and fifteen minutes the rotation was zero. The half-life period was seventy-eight minutes.

Unfortunately racemization tests in chloroform could not be performed since the active acids were soluble only in boiling solvent. The recrystallization of the active acids from chloroform indicated a more rapid racemization than in the other solvents.

l-2,2′-Dimethoxy-6,6′-dicarbomethoxydiphenyl.—In a side-arm test-tube was placed 1 cc. of thionyl chloride and 0.2 g. of l-2,2′-dimethoxy-6,6′-dicarboxydiphenyl having a rotation of −114.9'. The tube was stoppered and after standing at room temperature for two and one-half hours, the excess thionyl chloride was removed by suction. The residual acid chloride was treated with 3 cc. of absolute methyl alcohol and allowed to stand for two hours. The methyl alcohol was then evaporated and the crystalline ester was washed with 0.1 N sodium hydroxide and then with water. The I-ester melted at 101-102°.

Rotation. 0.0560 g. made up to 20 cc. in absolute methyl alcohol at 20° gave α −0.78°; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ −139". The solution was evaporated to the appearance of crystals. The material which separated had the same melting point and rotation.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.5; H, 5.45. Found: C, 65.7; H, 5.67.

d-2,2′-Dimethoxy-6,6′-dicarbomethoxydiphenyl.—The d-ester was prepared in a similar manner from a sample of d-acid having a rotation of +86.5°. The d-ester thus obtained melted at 98-99°.

Rotation. 0.0530 g. made up to 20 cc. in absolute methyl alcohol at 20° gave α_{D} +0.70°; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ +132°. The methyl alcohol was evaporated to the appearance of crystals. The material thus obtained had the same melting point and rotation.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.5; H, 5.45. Found: C, 65.64; H, 5.72.

Racemization Experiment

Rotation. 0.0508 g. made up to 20 cc. in glacial acetic acid at 20° gave α_{D} −0.886°; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ −174.5°. After refluxing for forty-five minutes the rotation was −122.5°; after three hours and fifty minutes, −27.6°; after five hours and fifty minutes, −11.8". Refluxing was then continued overnight to complete the racemization. The acetic acid was then evaporated and the ester thus obtained melted at 135–136° (the m. p. of the racemic ester). The half-life period was eighty-eight minutes.

l-2,2′-Dimethoxydiphenyl-6,6′-dicarboxylic Acid Amide.—The acid chloride prepared as described under the ester was poured slowly into 5 cc. of ice-cold aqueous ammonia (sp. gr. 0.9). Upon standing in the cold for six hours the amide separated as long needles which were filtered and dried. The l-amide melted at 230-231° (corr.).

Rotation. 0.0338 g. made up to 20 cc. in absolute methyl alcohol at 20" gave α −0.185"; l = 2; $[\alpha]^{20}_{\mathrm{D}}$ −54.8".

The amide was recrystallized from absolute methyl alcohol. The melting point and rotation were unchanged.

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: N, 9.33. Found: N, 9.33.

The d-amide obtained by a similar procedure melted at 230–231° (corr.).

Rotation. 0.0190 g. made up to 20 cc. in absolute methyl alcohol at 20° gave α_D $+0.102'$; $l = 2$; $[\alpha]^{20}_D$ $+53.6°$. The amide was recrystallized from absolute methyl alcohol. The melting point and rotation were unchanged.

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: N, 9.33. Found: N, 9.31.

Racemization Experiment

Rotation. 0.0582 g. of the I-amide made up to 20 cc. in glacial acetic acid at 20° gave α_D $-0.38''$; $l = 2$; $[\alpha]^{20}_D$ $-65.3'$. After refluxing for one hour and fifteen minutes the rotation was $-51.5''$; after four hours and fifteen minutes, $-29.2''$; after nine hours, $-17.2'$. Refluxing was then continued overnight, after which time the rotation was zero. The half-life period was four hours. The solvent was evaporated and the racemic amide thus obtained melted at 271–272°. A mixed melting point determination with racemic amide prepared from the racemic acid showed no depression.

2,2'-Dimethoxydiphenyl-6,6'-dicarboxylic Acid Amide.—The racemic amide was prepared from racemic 2,2'-dimethoxy-6,6'-dicarboxydiphenyl as described for the active acids, except that refluxing was necessary to form the acid chloride readily. The amide was recrystallized from 50% alcohol using norite. The melting point was 273–274°.

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: N, 9.33. Found: N, 9.48.

I-Nitro-2-iodo-3-carboxybenzene (I).[12]—This compound was produced by the method of Culhane and Whitmore in 65–75% yields.

I-Amino-2-iodo-3-carboxybenzene (II).—A solution of 320 g. of stannous chloride in 320 cc. of concentrated hydrochloric acid was warmed to 60°, and 40 g. of powdered 1-nitro-2-iodo-3-carboxybenzene was added with stirring. Sufficient ethyl alcohol (about 40 cc.) may be added with stirring if the reduction does not start (much larger amounts of alcohol caused diminution in yield). The mixture was stirred continuously and cooled sufficiently to maintain the temperature between 60 and 75°. After standing for an hour the mixture was cooled and the precipitated tin salt was removed by filtration with suction. The yield of double tin salt was 80 g. The run was repeated twice and the total 240 g. of double tin salt was treated with 750 cc. of water and sufficient aqueous ammonia to obtain an alkaline reaction. The mixture was heated to boiling, cooled and the curdy white precipitate of stannic oxide was removed by filtration with suction. The precipitate was washed with dilute aqueous ammonia and finally with water. The washings were added to the main portion and heated to boiling, cooled and filtered. The filtrate was made barely neutral with concentrated hydrochloric acid. The precipitated amino acid was filtered with suction and dried. The yield was 70.5 g. (68%). The crude product was purified by recrystallizing twice from 20% ethyl alcohol and formed purplish-gray needles, m. p. 133° (corr.). The amino acid was insoluble in cold but soluble in hot concentrated hydrochloric acid. On cooling, the hydrochloride of 1-amino-2-iodo-3-carboxybenzene crystallized out as fine granules which, when pure, start to decompose under 100" and finally melt with decomposition at 263–264°. The hydrochloride was readily soluble in water

Various attempts to reduce 1-nitro-2-iodo-3-carboxybenzene with ammoniacal ferrous sulfate were unsuccessful. The catalytic reductions with platinum black in hot and cold alcohol, ethyl acetate and glacial acetic acid all resulted in the formation of reddish, insoluble material. Catalytic reduction of the ethyl ester gave negative results. Reductions using zinc dust and acetic acid, and zinc dust and hydrochloric acid, were unsuccessful.

I-Fluoro-2-iodo-3-carboxybenzene (III).—To a solution of 100 cc. of 48% hydrofluoric acid at 25° in a platinum dish was added 42 g. of 1-amino-2-iodo-3-carboxy-

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(12) "Organic Syntheses," Collective Vol. I, 1932, p. 121.

benzene. After solution, the mixture was cooled to 0° by a salt–ice bath. This caused the formation of a gray pasty mass of the amine hydrofluoride. Then 11.5 g. of powdered sodium nitrite was added very slowly with continuous stirring. The precipitate dissolved with the formation of the diazonium fluoride, which was readily soluble. Diazotization was shown to be complete by a positive reaction with starch–potassium iodide paper five minutes after the addition of the last portion of sodium nitrite The diazotized solution was allowed to come to 30 ± 2° and remain at that temperature for two days. During this period bubbles of nitrogen were continually evolved from the solution and a precipitate slowly formed on the sides and bottom of the platinum vessel. The evolution of bubbles ceased after two days and the precipitate which had formed was removed by filtration with suction and washed with water. The yield was 28 g. (62.5%) of 1-fluoro-2-iodo-3-carboxybenzene which melted at 152–153° (corr.) after two crystallizations from water.

Anal. Calcd. for $C_7H_4O_2IF$: I, 47.76. Found: I, 47 37.

Diazotization of the amine in varying dilutions of hydrochloric acid solution with subsequent treatment with varying amounts of hydrofluoric acid or hydroborofluoric acid, or diazotization in hydrofluoric acid with subsequent addition of hydroborofluoric acid or diazotization in hydrofluoric acid with subsequent boiling with water gave a product soluble in alcohol or water, melting at 144–145" (corr.). This product was readily acetylated with acetic anhydride (whereas the fluoro compound melting at 152–153° was [illegible] similar treatment) to give a product insoluble in alcohol and water and melting at 144°. It is evident that the original compound is 1-hydroxy-2-iodo-3-carboxybenzene and the second the corresponding acetate.

1-Fluoro-2-iodo-3-carbomethoxybenzene (IV).—A mixture of 28 g of 1-fluoro-2-iodo-3-carboxybenzene and 19 g. of thionyl chloride was refluxed for ten hours. The excess of thionyl chloride was removed by distillation, 50 cc. of absolute methyl alcohol was added slowly and the mixture then refluxed for five hours. The excess alcohol was removed and the ester distilled under reduced pressure. The yield was 25 g. (85%) of a product boiling at 127–128° (4 mm.).

Anal. Calcd. for $C_8H_6O_2IF$: I, 45.33. Found: I, 44.93.

1-Fluoro-2-iodo-3-carboethoxybenzene.—A sample of 7 g. of 1-fluoro-2-iodo-3-carboxybenzene was similarly treated using absolute ethyl alcohol instead of methyl alcohol. The yield of ethyl ester was 6 g.; the boiling point was 148–150° (6 mm.).

Anal. Calcd. for $C_9H_8O_2IF$: I, 43.16. Found: I, 42.85.

2,2′-Difluoro-6,6′-dicarbomethoxydiphenyl (V).—To 28 g. of 1-fluoro-2-iodo-3-carbomethoxybenzene heated to 180° in a 100-cc. three-necked flask fitted with a stirrer and reflux condenser was added slowly with stirring 56 g. of copper powder. A vigorous exothermic reaction occurred after the addition of about half of the copper powder. The reaction mixture was heated at 240° for one hour. It was then cooled and the reaction mixture extracted five times with 50 cc. of ether The yield was 8.5 g. (57%). The product was crystallized from *p*-cymene and benzene to a constant melting point of 116–117°.

Anal. Calcd. for $C_{16}H_{12}O_4F_2$: C, 62.72; H, 3.95. Found: C, 62.45; H, 3.88.

2,2′-Difluoro-6,6′-dicarboethoxydiphenyl.—The diethyl ester was prepared similarly by the action of copper powder on 1-fluoro-2-iodo-3-carboethoxybenzene. Crystallization of the diethyl ester from *p*-cymene and then from absolute ethyl alcohol gave a product melting at 105–107°.

Anal. Calcd for $C_{18}H_{14}O_4F_2$: C, 64.64; H, 4.82. Found: C, 64.31; H, 4.64.

2,2′-Difluoro-6,6′-dicarboxydiphenyl (VI).—A mixture of 7.6 g. of dimethyl ester was saponified with an absolute ethyl alcohol solution of potassium hydroxide. Recrystallization from 95% ethyl alcohol raised the melting point to a constant value of 308–311° (corr.). The acid begins to shrink about 50" below the melting point recorded, softens noticeably about 10° below and melts sharply at the point given, forming a meniscus.

Anal. Calcd. for $C_{14}H_8O_4F_2$: C, 60.42; H, 2.90. Found: C, 60.18; H, 2.99. Neut. equiv.: calcd., 278.1. Found: 280.0.

Resolution **of 2,2′-Difluoro-6,6′-dicarboxydiphenyl.**—To a hot solution of 2.5 g. of 2,2′-difluoro-6,6′-dicarboxydiphenyl in 75 cc. of 95% ethyl alcohol was added with stirring a hot solution of 3.0 g. of anhydrous quinine in 45 cc. of 95% ethyl alcohol. The solution was evaporated to 95 cc. and allowed to cool. A crop of white flaky crystals separated, which was essentially pure salt, as shown by rotation and melting point as compared with recrystallized material. The crystals of pure less soluble salt were removed by filtration with suction, washed with 95% alcohol and dried; weight 2.5 g. Recrystallization from 95% ethyl alcohol gave a pure product of melting point 221–222° (corr.).

Rotation. 0.1695 g. made up to 15 cc. with absolute ethyl alcohol at 20° gave α_D +0.44°; $l = 1$; [a]: +38.9°. Recrystallization from 95% ethyl alcohol did not change the melting point or rotation.

Anal. Calcd. for $C_{34}H_{32}O_6F_2N_2$: N, 4.65. Found: N, 4.52.

The mother liquor from the first crop of crystals was further evaporated to 50 cc. Upon cooling, 0.32 g. of salt crystallized out, which was by rotation shown to be impure less soluble salt. The filtrate was evaporated to dryness and the residue of more soluble salt washed once with 25 cc. of a 10% solution of ethyl alcohol in water. After drying, the weight was 2.5 g. and the melting point was 159–160" (corr.).

Rotation. 0.1755 g. made up to 15 cc. with absolute ethyl alcohol at 20° gave α_D −1.18°; $l = 1$; [a]: −101°. The more soluble salt was dissolved in ethyl alcohol and precipitated by the addition of water into two fractions. The melting point was unchanged and the rotation of the two fractions identical with that of the original material.

Anal. Calcd. for $C_{34}H_{36}O_6F_2N_2$: N, 4.65. Found: N, 4.32.

l-2,2′-Difluoro-6,6′-dicarboxydiphenyl.—The pure less soluble salt was hydrolyzed by two procedures, both giving practically the same results. The first procedure consisted in digesting 1.0 g. of salt three times for ten minutes each in the cold with 10 cc. of 2 N hydrochloric acid. The pasty mass which first formed changed to white flakes on' continued stirring. The active l-acid so obtained was then washed on a filter with another 10-cc. portion of 2 N hydrochloric acid, then with water, and finally crystallized from 95% ethyl alcohol. The melting point was 305–306° (corr.), with a melting behavior similar to that of the racemic acid. A mixed melting point with the racemic acid gave 302–304° (corr.).

Rotation. (a) 0.1535 g. made up to 15 cc. with 95% ethyl alcohol at 20° gave α_D −0.23"; $l = 1$; $[\alpha]^{20}_D$ −22.5'. (b) 0.1008 g. made up to 15 cc. with 0.1 N sodium hydroxide at 20° gave α_D −0.835'; $l = 1$; $[\alpha]^{20}_D$ −124°.

The second procedure consisted in digesting 1.2 g. of pure less soluble salt with 10 cc. of cold 2 N hydrochloric acid for five minutes. The acid was decanted and the white flakes which were obtained from the pasty mass by stirring were washed with water and dissolved in 2 N sodium hydroxide solution. The solution was warmed to 80°, immediately cooled, and extracted three times with 4 cc. each of chloroform. The alkaline solution was then acidified with concentrated hydrochloric acid. The l-acid precipitated and was washed with water and dried. After crystallization from 95% ethyl alcohol, the melting point was 305–306° (corr.).

Rotation. 0.0945 g. made up to 15 cc. with 0.1 N sodium hydroxide at 20° gave α_D −0.8'; $l = 1$; $[\alpha]^{20}_D$ −127.0".

Anal. Neut equiv., calcd., 278.1. Found: 280.

d-**2,2'-Difluoro-6,6'-dicarboxydiphenyl.**—The d-acid was obtained from 2 2 g. of the more soluble salt by the second procedure given above. After recrystallization from 95% ethyl alcohol the melting point was 305–306° (corr).

Rotation. (a) 0.1387 g. made up to 15 cc. with 0.1 *N* sodium hydroxide at 20° gave α_D +0.94°; 1 = 1; $[\alpha]^{20}_D$ +101.8°. (b) 0 1071 g. made up to 15 cc. with 95% ethyl alcohol at 20° gave α_D +0.12"; *l* = 1; $[\alpha]^{20}_D$ +16.8°.

Synthesis of More Soluble Salt.—An alcohol solution of 0 1071 g. of d-acid having a rotation in alcohol of +16.8° was treated with 0.125 g. of quinine. The salt obtained upon evaporation of the alcohol to 2 cc. and precipitation with water was washed with water and dried. The melting point was 163–165° (corr.).

Rotation. 0.0860 g. made up to 15 cc. with absolute ethyl alcohol at 20° gave α_D −0.435°; *l* = 1; $[\alpha]^{20}_D$ −76.0°.

Racemization Experiments

In Sodium Hydroxide—Hot.—The rotation was taken on an alkaline solution of the I-acid. *Rotation.* 0.0945 g. made up to 15 cc. with 0.1 N sodium hydroxide at 20° gave α_D −0.8"; *l* = 1; $[\alpha]^{20}_D$ −127°. The alkaline solution was heated in a closed container on a steam cone for eight minutes. The rotation was again taken and the acid was found to be completely racemized.

In Sodium Hydroxide—Cold.—The rotation was taken on an alkaline solution of partially active 1-acid. *Rotation.* 0.0870 g. made up to 15 cc. with 0.1 N sodium hydroxide at 20° gave α_D −0.38°; *l* = 1; $[\alpha]^{20}_D$ −66.5°. After standing for one day at room temperature (25°) the rotation was −60°, after two days, −54°, after three days, −45°, after five days, −24°, and after one week the rotation was −18°. A solution of d-acid in 0.1 N sodium hydroxide racemized from a rotation of +62.3° to +15° after standing at 25° for one week.

In Ethanol.—A solution of I-acid was made in 95% ethyl alcohol. *Rotation.* 0.0892 g. made up to 15 cc. with 95% ethyl alcohol at 20° gave α_D −0.12"; *l* = 1; $[\alpha]^{20}_D$ −20.2". The alcoholic solution was refluxed for one hour and the rotation was then −11.7°. The solution was refluxed an additional hour and a half and the rotation was zero.

In Acetic Anhydride.—A sample of 0.1014 g. of acid having a rotation of −127° in 0.1 N sodium hydroxide was dissolved in 15 cc. of acetic anhydride. Warming to 50° for three minutes was required to effect solution. The rotation in acetic anhydride was taken and found to be zero. The solution was boiled for ten minutes and the acetic anhydride removed in a vacuum. The residue was dissolved in 0.1 N sodium hydroxide. It was necessary to bring the mixture to boiling to effect solution as the residue went into solution very slowly. The solution was immediately cooled and the rotation in 0.1 N alkali was zero.

In Acetic Acid.—A 0.1281-g. portion of acid having a rotation of −66.5° in 0.1 *N* alkali was dissolved in 15 cc. of glacial acetic acid. Solution took place readily in the cold and the rotation was found to be zero. The acetic acid solution was refluxed for five minutes and the acetic acid removed in a vacuum. The residue dissolved readily in cold 0.1 N sodium hydroxide. The rotation in 0.1 N alkali was found to be −36.6". Refluxing with glacial acetic acid, therefore, caused partial racemization.

In Alcoholic Hydrochloric Acid.—A solution of d-acid was prepared with absolute ethyl alcohol containing 40% concentrated hydrochloric acid. *Rotation.* 0.1181 g. made up to 15 cc. with absolute ethyl alcohol containing 40% of hydrochloric acid at 20° gave α_D +0.09°; 1 = 1; $[\alpha]^{20}_D$ +11.4°. After standing for one week the rotation was +6.6°.

Summary

1 2,2′-Difluoro-6,6′-dicarboxydiphenyl has been prepared from 1-methoxy-2-iodo-3-carboxybenzeneby reduction to the amine, diazotization and replacement of the amino group by fluorine, and coupling by means of copper powder.

2. The compound has been resolved into optical isomers through the quinine salt. The active forms of 2,2′-difluoro-6,6′-dicarboxydiphenyl racemize rapidly in hot dilute alkali, fairly readily in hot alcohol, hot acetic anhydride or hot glacial acetic acid, and slowly in cold dilute alkali or in a 40% solution of concentrated hydrochloric acid in absolute alcohol.

3. 2,2′-Dimethoxy-6,6′-dicarboxydiphenyl has been prepared and resolved according to the outlined procedure of Kenner and Turner. The active acids racemized much more slowly than the difluoro compounds.

4. The active 2,2′-dimethoxy-6,6′-dicarbomethoxydiphenyl and the corresponding methyl ester racemized at about the same rate. The active diamide racemized much more slowly.

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

Stereochemistry of Diphenyl. XXVIII.[1] Preparation and Properties of 2,2′-Difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl

BY E. C. KLEIDERER[2] AND ROGER ADAMS

Diphenyls containing fluorine in one or more of the 2,2′,6,6′-positions are of especial interest in connection with the stereochemistry of the diphenyls, since fluorine is the smallest substituent which can be introduced in place of a hydrogen. The compounds of this type thus far prepared are the non-resolvable 2,2′-difluoro-3,3′-dicarboxy-6,6′-dimethoxydiphenyl[3] (I), the extremely unstable brucine salt of 2-nitro-6-carboxy-2'-fluorodiphenyl[4] (11), the easily racemized 2,2′-difluoro-3,5,3′,5′-tetramethyl-6,6′-diaminodiphenyl[5] (III) and 2,2′-difluoro-6,6′-dicarboxydiphenyl[1] (IV). Although the properties of these compounds agree satisfactorily with those predicted for such structures, nevertheless, it might appear that the mobility of these compounds may be due to some specific property of the fluorine, other than its small size. A compound has, therefore, been

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[1] For paper XXVII see Stanley, McMahon and Adams, THIS JOURNAL, 66, 706 (1933).

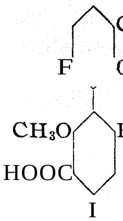
[2] The experimental work was done by E. C. Kleiderer in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Becker and Adams, THIS JOURNAL, 64, 2973 (1932).

[4] Stoughton and Adams, *ibid.*, 54, 4426 (1932).

[5] Kleiderer and Adams, *ibid*, 64, 1575 (1932).

synthesized containing 2,2′-difluoro substitution and 6,6′-disubstitution with nitro groups which are relatively large.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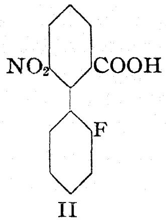
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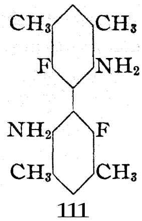
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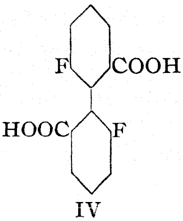
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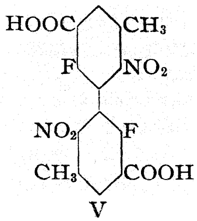
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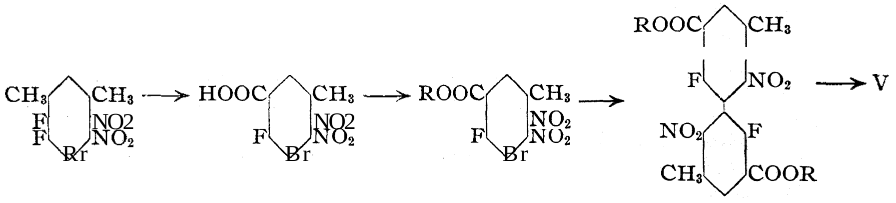
This should be resistant to racemization if the size of the groups is the primary influence, and it, indeed, proved to be so. This is satisfactory evidence that the lability of all the previously studied fluorodiphenyls is due, primarily, to the size rather than to any other specific property of the fluorine atom.

The compound prepared was 2,2′-difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl (IX). The l-form showed no appreciable racemization after several hours of boiling in ethyl alcohol, glacial acetic acid, cyclohexanone and 0.1 N sodium hydroxide. The alkaline solution, however, became colored on standing and an extended experiment in this solvent was impossible.

Experimental

The dinitro-difluoro compound was prepared by the following series of reactions


VI VII VIII

1-Bromo-2-fluoro-3-carboxy-5-methyl-6-nitrobenzene (VI).—A mixture of 5 g. of 1-bromo-2-fluoro-3,5-dimethyl-6-nitrobenzene[5] (V) and 20 cc. of concentrated nitric acid (sp. gr. 1.42) diluted with 40 cc. of water, was placed in a sealed tube and heated in a horizontal position for eight hours at 150" (Longer than eight hours gave considerable decomposition with evolution of carbon dioxide.) Upon cooling, the reaction mixture was made alkaline, filtered and extracted once with ether. Upon acidification with dilute sulfuric acid, the acid precipitated as a light yellow curd. The crude acid was crystallized from dilute alcohol. It formed light yellow needles melting at 249–251" (corr.). In no case was a mixture of acids obtained. The yield was 2 g. (36% of the theoretical).

Anal. Calcd. for $C_8H_5O_4BrFN$: N, 5.04; Br, 28.80; neut. equiv., 278. Found: (micro Dumas) N, 5.34; Br, 28.89; neut. equiv , 275.3.

The evidence that the methyl group adjacent to the fluorine was oxidized and not that adjacent to the nitro was indirect. By the same concentration of nitric acid and under the same conditions used in the oxidation just described, it was found that in 1-

nitro-2,4-dimethylbenzene, the 4-methyl group oxidized exclusively. The methyl ortho to the nitro apparently was unaffected by this reagent.

1-Bromo-2-fluoro-3-carbomethoxy-5-methyl-6-nitrobenzene (VII).—VI was heated with excess of thionyl chloride for five minutes to convert it to the acid chloride. The crude acid chloride was treated with absolute methyl alcohol and refluxed for thirty minutes. The ester was isolated by pouring the methyl alcohol mixture onto ice. It was purified by crystallization from 50% methyl alcohol, from which it crystallized in white needles melting at 88–89" (corn.). The yield was quantitative.

Anal. Calcd. for $C_9H_7O_4BrFN$: N, 4.80. Found: (micro Dumas) N, 4.73.

1-Bromo-2-fluoro-3-carboethoxy-5-methyl-6-nitrobenzene (VII).—The ethyl ester was prepared in the same way as the methyl ester. The ester was purified from 50% ethyl alcohol, from which it crystallized in white needles melting at 65–66° (corr.). The yield was quantitative.

Anal. Calcd. for $C_{10}H_9O_4BrFN$: N, 4 58. Found: (micro Dumas) N, 4.46.

2,2′-Difluoro-3,3′-dicarbomethoxy-5,5′-dimethyl-6,6′-dinitrodiphenyl (VIII).—In a large Pyrex test-tube a mixture of 4.8 g. of (VII) and 5 g. of copper bronze was heated to 225°, when the reaction began as evidenced by the change in color of the copper. The reaction was allowed to continue at 220" for one hour. The melt was extracted with acetone and the solution treated with activated carbon (norite). The essentially colorless acetone was evaporated slowly and absolute methyl alcohol added. After most of the acetone had evaporated the diphenyl compound crystallized in needles, melting upon recrystallization from methyl alcohol at 191–193° (corr.). The yield was 2.26 g. (65%).

Anal. Calcd. for $C_{18}H_{14}O_8F_2N_2$: N, 6.60. Found: (micro Dumas) N, 6.79.

2,2′-Difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl (V).—A mixture of the ester (VIII), 50% methyl alcohol and a slight excess of sodium hydroxide over that necessary for hydrolysis, was refluxed for thirty minutes, at which time the diester had dissolved and the solution had changed from colorless to light yellow. After cooling, acidifying, evaporating to half volume and again cooling the acid crystallized in short colorless needles. These were recrystallized from 50% ethyl alcohol. They melted at 301–304" (uncorr.) on the bloc Maquenne, 318–320° (corr.) with decomposition in a melting-point tube.

Anal. Calcd. for $C_{16}H_{10}O_8F_2N_2$: N, 7.07; neut. equiv., 198. Found: (micro Dumas) N, 7.15; neut. equiv., 196.5.

Resolution **of 2,2′-Difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl** (V.) Strychnine Salt.—To a solution of 2.1 g. of strychnine dissolved in 300 cc. of absolute methyl alcohol was added 1.23 g. of the acid (V). The solution was evaporated to 210 ce. and allowed to stand overnight in a'desiccator. At the end of this time 1.5 g. of salt had crystallized.

The salt for purification was dissolved in 150 cc. of absolute methyl alcohol and allowed to stand overnight. At the end of this time the salt had crystallized out in small cubes. The melting point was 224–228° (corr), with decomposition.

Rotation. 0.1000 g. made up to 10 cc. with pyridine at 20° gave α_D −0.75°, l = 1; $[\alpha]^{20}_D$ −75°. Further recrystallization brought no change in rotation.

Anal. Calcd. for $C_{16}H_{10}O_8F_2N_2 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.89. Found: (micro Dumas) N, 7.83.

The mother liquor from the first crop of crystals was evaporated to 150 cc., when 0.35 g. of needle-like crystals came down. These were filtered off and the filtrate was evaporated to 80 cc. and allowed to stand overnight. At the end of this time 1 g. of needle-like crystals had separated. This last fraction was recrystallized from absolute methyl alcohol, m. p. 190–193° (corr.) with decomposition.

Rotation. 0.1000 g. made up to 10 cc. with pyridine at 20° gave α_D −0.50, 1 = 1; $[\alpha]^{20}_{D}$ −50.0°. Further recrystallization gave no change in rotation.

Anal. Calcd. for $C_{16}H_{10}O_8F_2N_2 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.89. Found: (micro Dumas) N, 7.56.

As the nitrogen analysis will not distinguish the mono- and distrychnine salts, a portion of salt was decomposed quantitatively and acid and base isolated. The salt proved to be dibasic.

0.2230 g. of salt yielded 0.0830 g. of acid and 0.1350 g. of strychnine. For 0.0830 g of acid, there is required 0.1400 g. of strychnine for a dibasic salt.

***l*-2,2′-Difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl.**—The less soluble salt was treated in the cold with 5% aqueous sodium hydroxide for about thirty minutes. At the end of this time the precipitated strychnine was filtered off. The acid was precipitated with dilute hydrochloric acid and purified from 50% alcohol, from which it crystallized in white needles. The melting point (tube) was 298–300° (corr.) with decomposition.

Rotations. 0.1000 g. made up to 10 cc. at 20° with methyl alcohol gave α_D −0.17°, l = 1; $[\alpha]^{20}_{D}$ −17.0°.

Further recrystallization did not change the rotation.

0.0750 g. made up to 10 cc. at 20° with pyridine gave α_D −0 18°, 1 = 1; $[\alpha]^{20}_{D}$ −24 0°.

0.1000 g. made up to 10 cc. at 25° with cyclohexanol gave α_D −0.12°, l = 1; $[\alpha]^{20}_{D}$ −12.0°.

0.1000 g. made up to 10 cc. at 20° with glacial acetic acid gave a, −0.15°, 1 = 1; $[\alpha]^{20}_{D}$ −15.0'.

0.1068 g. made up to 10 cc. at 20° with cyclohexanone gave a, −0.154°, 1 = 1; $[\alpha]^{20}_{D}$ −14 4°.

0.1000 g. made up to 10 cc. at 20° with 0.1 Nsodium hydroxide gave a, −0.135°, l = 1; $[\alpha]^{20}_{D}$ −13.5°.

Anal. Calcd. for $C_{16}H_{10}O_8F_2N_2$: N, 7.07. Found: (micro Dumas) N, 7.17.

***d*-2,2′-Difluoro-3,3′-dicarboxy-5,5′-dimethyl-6,6′-dinitrodiphenyl.**—The d-acid was prepared in the same way as the 1-isomer. After crystallization from 50% alcohol it melted at 297–301° (corr.) with decomposition.

Rotation. 0.1000 g. made up to 10 cc. at 20° with methyl alcohol gave a, +0.15°, l = 1; $[\alpha]^{20}_{D}$ +15.0°.

Anal. Calcd. for $C_{16}H_{10}O_8F_2N_2$: N, 7.07. Found: (micro Dumas) N, 7.11.

Racemization Experiments.—Refluxing in 95% ethyl alcohol for five hours; in glacial acetic acid for seven hours; in cyclohexanone for three hours; in 0.1 N sodium hydroxide for three hours resulted in no appreciable change in rotation.

Summary

1. 2,2′ - Difluoro - 3,3′ - dicarboxy - 5,5′ - dimethyl - 6,6′ - dinitrodiphenyl has been synthesized and resolved. The probable presence of the two carboxyl groups as 3,3′ and not 5,5′ was determined only by indirect evidence.

2. The active forms are stable to racemization under the conditions used. This is evidence that the mobility of previously prepared fluoro derivatives is due not to any peculiar property of the fluorine atom but probably primarily to its size.

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

The Coupling Action of the Grignard Reagent. IV. Benzal Chloride and Benzotrichloride

BY REYNOLD C. FUSON AND WM. E. ROSS

It has been shown previously that the benzyl halides when treated with methylmagnesium iodide are converted into dibenzyl according to the equation: $2C_6H_5CH_2X + 2CH_3MgI = CH_3CH_3 + C_6H_5CH_2CH_2C_6H_5 + 2MgIX$.[1] This type of reaction has been reported by several investigators and appears to be applicable to a rather wide variety of types of halogen compounds. An examination of these various compounds, however, reveals the striking fact that the most conspicuous examples contain the skeletal grouping, $Ar-\overset{|}{\underset{|}{C}}-X$, characteristic of arylmethyl halides. Thus, for example, the methoxybenzyl halides,[2] di-α-naphthylmethylchloromethane,[3] diphenylbromoethane,[2] ethylphenylbromomethane,[2] α - chlorophenylacetic acid[4] and the cyanobenzyl halides[5] give the coupling reaction and all of them possess the structural grouping in question.

On the other hand, benzal chloride and benzotrichloride—compounds which contain this structural unit—have not been found to undergo coupling. Reychler[6] examined the behavior of these two compounds toward phenylmagnesium bromide. In the case of benzotrichloride, he was unable to isolate any definite products. Benzal chloride gave a large amount of triphenylmethane and a small quantity of s-tetraphenylethane. Reychler attributed the formation of the latter to the action of metallic magnesium on diphenylchloromethane formed as an intermediate. In the light of Spath's work on diphenylbromomethane, we would now explain Reychler's result as due to the coupling of diphenylchloromethane by the action of the Grignard reagent.

In view of the fact, already pointed out, that benzal chloride and benzotrichloride possess the structural grouping which seems to be most effective in promoting the coupling tendency, the behavior of these two compounds toward the Grignard reagent has been reëxamined. The present paper is a report of this investigation.

Benzal Chloride.—In the case of benzal chloride methylmagnesium iodide was chosen as the reagent because of the high yields of coupling products which this reagent was found to give when used with the benzyl halides and with the cyanobenzyl halides. The results obtained were altogether unlike those reported by Reychler for phenylmagnesium

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(1) Fusou, THIS JOURNAL, 48, 2937 (1926).

(2) Späth, *Monatsh.*, 34, 1965 (1913).

(3) Schmidlin and Massini, *Ber.*, 42, 2384 (1909).

(4) MacKenzie, Drew and Martin, *J. Chem. Soc.*, *107*, 26 (1915).

(5) Fuson, THIS JOURNAL, 48, 830 (1926)

(6) Reychler, Bull. *soc. chim.*, *35*, *737* (1906)

bromide and benzal chloride. It was found that methylmagnesium iodide effected direct coupling just as it did in the case of benzyl chloride, the second chlorine atom apparently having no influence upon the course of the reaction. The product was α-stilbene dichloride and the equation representing the reaction is

$$2C_6H_5CHCl_2 + 2CH_3MgI \longrightarrow C_6H_5CHClCHClC_6H_5 + CH_3CH_3 + 2MgICl$$

No evidence was obtained of the formation of cumene or of *s*-dimethyldiphenylethane—the products which would have been predicted in analogy with Reychler's results.[7] In view of this fact the reaction between benzal chloride and phenylmagnesium bromide has been reexamined. As in Reychler's work, triphenylmethane was obtained, but no *s*-tetraphenylethane was isolated. Instead, considerable amounts of diphenyl and α-stilbene dichloride were found. These products evidently arise from the following reaction—a typical example of coupling

$$2C_6H_5CHCl_2 + 2C_6H_5MgBr = C_6H_5CHClCHClC_6H_5 + C_6H_5-C_6H_5 + 2MgBrCl$$

Benzotrichloride.—The Grignard reagent used in connection with the study of benzotrichloride was methylmagnesium chloride. Experiments were carried out with dilute solutions (0.2 molal) and with concentrated solutions (2 molal). In the presence of the dilute reagent benzotrichloride underwent coupling to yield tolane tetrachloride as shown by the equation

$$2C_6H_5CCl_3 + 2CH_3MgCl = C_6H_5CCl_2CCl_2C_6H_5 + CH_3CH_3 + 2MgCl_2$$

The reaction between benzotrichloride and the concentrated solution of methylmagnesium chloride gave an entirely different result. No tolane tetrachloride was isolated and instead there was obtained a mixture of the cis and *trans* forms of tolane dichlorides. The total yield of these isomers was about 22% of the theoretical; the proportion of the *trans* form to the cis was approximately 5 to 1.

It seemed probable that the effect of the concentration of the reagent was due not to a difference in the initial coupling reaction but to a difference in the stability of the initial product, tolane tetrachloride, toward the two solutions of the reagent. If this surmise were correct the tetrachloro compound which was stable in the dilute solution of the reagent should be attacked by the concentrated solution. Experiment has verified this hypothesis In the 2 molal solution of methylmagnesium chloride tolane tetrachloride was found to react to give a mixture of the two geometrically isomeric tolane dichlorides.

Experimental

The Reaction of Benzal Chloride with Methylmagnesium Iodide.—To an approximately 2 molal solution of methylmagnesium iodide (prepared from 60 g. of methyl io-

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[7] Since this work was done experiments have been carried out with benzal chloride and methylmagnesium chloride with results which are somewhat more in accord with those of Reychler. Evidence is now available which indicates that the halogen involved in the Grignard reagent used has a profound influence on the course of the reaction. A report of this work will appear in the near future.

dide and 10 g. of magnesium) was added over a period of two hours with continuous stirring 25 g. of benzal chloride. The reaction was very vigorous and caused the ether solution to boil steadily throughout the time of reaction. The stirring was discontinued and the reaction mixture was then heated externally and the boiling was maintained for two hours longer. Following this, the mixture was decomposed with concentrated hydrochloric acid and ice.

The supernatant ether layer was then separated and washed with a solution of sodium thiosulfate to remove any free iodine, and the ether was then evaporated by drawing a stream of air over the surface of the solution. The semi-solid residue which remained was separated by means of a suction filter into a colorless crystalline solid and a brown viscous oil. The yield of the solid before recrystallization was 4.3 g.

After three recrystallizations from glacial acetic acid the solid was obtained in large, colorless prisms melting at 189–190°. A mixture of this compound with α-dichlorostilbene (melting point 190°)[8] melted at 190°.

The brown, viscous oil did not crystallize and could not be distilled even at 200° at 10 mm. No evidence was obtained of the presence of cumene.

The Reaction of Benzal Chloride with Phenylmagnesium Bromide.—A mixture of 150 cc. of a 1.6 molal solution of phenylmagnesium bromide and 32 g. of benzal chloride was heated under reflux. A crystalline precipitate began to separate almost immediately and at the end of three hours the liquid contained a large amount of suspended solid. Water and hydrochloric acid were added until two clear layers resulted. The ether layer was separated and the ether was removed on the steam-bath. The residue was a brown, lachrymatory oil which when cooled in an ice-bath deposited crystals melting at 190–192° after one recrystallization from glacial acetic acid. A mixture of these crystals with α-stilbene dichloride melted at 190–192°.

The remainder of the oily material was subjected to distillation. Ten grams of unchanged benzal chloride was recovered. A considerable amount of diphenyl was also removed during the distillation. The tarry residue deposited crystals which were filtered and recrystallized from ethyl alcohol. A mixed melting point determination showed this compound to be triphenylmethane (melting point 92°).

The Reaction of Benzotrichloride with Methylmagnesium Chloride in Dilute Solution.—To 500 cc. of an approximately 0.2 molal solution of methylmagnesium chloride in ether was added slowly 19.5 g. of benzotrichloride in 50 cc. of anhydrous ether. There was no evidence of a reaction. The mixture was then heated under reflux with continued stirring for three hours. Decomposition of the reaction mixture with water and hydrochloric acid and subsequent distillation of the ether from the ether layer gave a brown oil. This material was placed in a 10% solution of sodium hydroxide and subjected to steam distillation. About 3 cc. of unchanged benzotrichloride was recovered in the distillate. A crystalline substance was left in the distilling flask. After six recrystallizations from glacial acetic acid this compound melted at 161–162°. One gram of the pure compound was obtained in the form of a fine, white powder. A mixture of this compound with an authentic specimen of tolane tetrachloride (melting point, 161–162°)[9] showed no depression in the melting point.

The Reaction of Benzotrichloride and Methylmagnesium Chloride in Concentrated Solution.—To 200 cc. of an approximately 2 molal solution of methylmagnesium chloride was slowly added[10] 39 g. of benzotrichloride. Although the addition was carried out in a dropwise manner it caused the ether to boil vigorously. After the addition was complete and the reaction had apparently ceased, the mixture was heated under

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(8) Zincke, Ber., 10, 1002 (1877).

(9) Zinin, Ann., 34, 188 (1840).

(10) This as well as other solutions of methylmagnesium chloride used in these experiments was analyzed by titration with acid.

reflux for an hour. The mixture was decomposed in the manner described for the experiment which was carried out in dilute solution. Also, the steam distillation was conducted in the way described for the preceding experiment. However, the distillate in this case came over very slowly. In addition to a few cc. of oil the distillate contained a waxy solid which was collected over a period of eighteen hours of continued distillation. This material was a mixture of *cis* and *trans* tolane dichlorides. The two isomers were separated by fractional crystallization from alcohol. The *trans* isomer melted at **63"** and the *cis* form at **138–139°**. In several experiments there was obtained an average yield of 22% of that theoretically possible for the two dichlorides. The proportion of *cis* to *trans* was about **1** to **5.**

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, *28.5*. Found for the *cis* isomer: Cl, *28.5*. Found for the *trans* isomer: Cl, *28.6*.

The Reaction between Methylmagnesium Chloride and **Tolane Tetrachloride.**—Seven-tenths gram of tolane tetrachloride was heated under reflux for four hours with an excess of a 2 molal solution of methylmagnesium chloride. Decomposition of the reaction mixture in the usual manner gave a solid melting from *63* to 80° which proved to be a mixture of the isomeric tolane dichlorides. The yield was *0.2* g.

Summary

Methylmagnesium iodide has been shown to exert a coupling action on benzal chloride. The product, α-stilbene dichloride (C_6H_5CHCl-$CHClC_6H_5$), was likewise obtained when phenylmagnesium bromide was allowed to react with benzal chloride.

A similar coupling was observed with benzotrichloride. When treated with a dilute solution of methylmagnesium chloride it gave tolane tetrachloride ($C_6H_5CCl_2CCl_2C_6H_5$).

In concentrated solutions of methylmagnesium chloride benzotrichloride has been found to yield a mixture of the cis and *trans* forms of **tolane dichloride** ($C_6H_5CCl{=}CClC_6H_5$).

The same mixture of isomers was obtained when tolane tetrachloride was treated with the concentrated solution of methylmagnesium chloride.

The latter result has been interpreted to mean that tolane tetrachloride is produced alike by dilute and by concentrated solutions of the reagent but that in the latter case it is subsequently transformed into the tolane dichlorides.

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Reduction Studies of Schiff Bases. III. The Condensations of Certain Secondary Aromatic Amines with Formaldehyde in Acid Solution; Nuclear or N-Methylations by Means of Formaldehyde

BY E. C. WAGNER

Condensations of formaldehyde and other aldehydes with aromatic amines in neutral or alkaline media yield compounds of either the azomethine or the di-imine type. A similarly simple statement cannot be made regarding condensations in acid media. There is scattered evidence, mostly for negatively substituted aldehydes or amines,[1] that in any case the initial step is the additive union of aldehyde and amine, but the actual existence of intermediate addition compounds has been demonstrated in only a few instances, owing to the ease with which the condensation is usually completed by loss of a molecule of water. From acid media the azomethine or di-imine is obtained in some cases,[2] but in general, though a trace of acid may catalyze condensation,[3] presence of mineral acid may promote the reverse hydrolysis, or, especially in the case of formaldehyde, may lead to further changes, with the result that the first isolable product is of secondary origin. Such secondary products may be designated as of (1) the anhydro-aminobenzyl alcohol type, (2) the less important intermediate aminobenzylaniline type[4] and (3) the diaminodiphenylmethane type, the last representing the final stage, since compounds of this type are obtainable not only from the first two,[4,5] but from the azomethines, the di-imines,[6] or without the appearance of intermediate stages, from the amines.[7] Of the three types whose formation is peculiar to condensations in acid media it seems probable that the anhydro-aminobenzyl alcohol type forms first.[6e,4c] The mechanism of its formation is therefore important in a study of condensations of formaldehyde and aromatic amines in acid media, and several investigations have been made of this matter.

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(1) Wheeler and Jordan, THIS JOURNAL, **31**, 937 (1909); Dimroth and Zoeppritz, *Ber.*, **35**, 984 (1902); Rügheimer, *ibid.*, **39**, 1653 (1906); Lowy and Balz, THIS JOURNAL, **43**, 341 (1921); Kondo and Ishida, *J. Pharm. Soc. Japan*, **489**, 979 (1922); *Chem. Abstracts*, **17**, 1456 (1923).

(2) Tröger, *J. prakt. Chem.*, [2] **36**, 225 (1887); Haegele, *Ber.*, **25**, 2753 (1892); Walther and Kausch, *J. prakt. Chem.*, [2] **56**, 111 (1897); Möhlau, *Ber.*, **31**, 2250 (1898); Dimroth and Zoeppritz, Ref. 1; Lowy and Westcott, THIS JOURNAL, **42**, 849 (1920); Lowy and Downey, *ibid.*, **43**, 346 (1921); Lowy and Balz, Ref. 1; Lowy and King, *ibid.*, **43**, 625 (1921); **46**, 757 (1924); Shimo, *Bull. Chem. Soc. Japan*, **1**, 202 (1925); *Chem. Zentr.*, I, 597 (1927); Levi, *Gazz. chim. ital.*, **59**, 544 (1929).

(3) Reddelien, *Ber.*, **46**, 2718 (1913).

(4) (a) German Patent 87,934; *Friedl.*, **4**, 66; (b) Maffei, *Gazz. chim. ital.*, **58**, 261 (1928); (c) Meyer and Stillich, *Ber.*, **35**, 739 (1902).

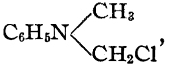
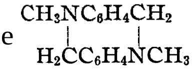
(5) German Patent 83,544; *Friedl.*, **4**, 50; German Patent 97,710; *Friedl.*, **5**, 94.

(6) (a) German Patent 53,937; *Friedl.*, **2**, 53; (b) Patent 58,072 *Friedl.*, **3**, 79; (c) Patent 70,402; *Friedl.*, **3**, 80; (d) v. Braun, *Ber.*, **41**, 2145 (1908); (e) Meyer and Rohmer, *ibid.*, **33**, 250 (1900); (f) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894).

(7) German Patent 68,011; *Friedl.*, **3**, 91; Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929).

A mechanism proposed in a Kalle and Co. patent[8] is represented thus:

$$C_6H_5NH_2HCl + CH_2O \longrightarrow \boxed{H}C_6H_4NHCH_2\boxed{Cl} \xrightarrow{\text{alkali}} \underbrace{CH_2C_6H_4NH}_{} \text{ (polymerized)}$$

Green and Saunders[9] suggested a similar course, the chloromethyl compound yielding momentarily the corresponding hydroxymethyl compound. The actuality of the chloromethyl compounds does not seem to be established, though analogous compounds such as $C_6H_5NHCH_2CN$, etc., are known. The crystalline and definite compounds obtained from methylaniline and ethylaniline, and represented[10] to be chloromethyl compounds, *e. g.*,  $C_6H_5N\begin{smallmatrix}CH_3\\CH_2Cl\end{smallmatrix}$, were shown by Friedländer[11] to be hydrochlorides of the dimeric anhydro-alkylaminobenzyl alcohols, the structure being proved, in the case of the methyl compound, by reduction to *p*-toluidine. Friedlander concluded that formaldehyde first unites at the para-position to yield the carbinol $CH_3NHC_6H_4CH_2OH$, of which two molecules condense with loss of water to yield the dimeric base  $\begin{matrix}CH_3NC_6H_4CH_2\\ | \qquad\quad |\\ H_2CC_6H_4NCH_3\end{matrix}$ whose dihydrochloride appears as product.

This view seems to be inconsistent with the ready formation of the anhydro-aminobenzyl alcohols from azomethines or di-imines, and with the claims of several patents[12] on N-alkylation of aromatic amines by condensation with homologs of formaldehyde, with concurrent reduction, in acid solution, indicating that the primary point of attack is the nitrogen atom. This is also the basis for the mechanism recently proposed for similar condensations by v. Braun and co-workers,[13] involving the assumed primary formation of a N-hydroxyalkyl compound, *e.* g., $C_6H_5NR_2Cl$ $CH(OH)R$, which rearranges to the form $\underbrace{RCHC_6H_4NR_2Cl}_{}$.

The present study deals with the condensations of five alkylanilines (methyl, ethyl, n-propyl, n-butyl and isoamyl) with formaldehyde in dilute hydrochloric or sulfuric acid solution. Two series of experiments were made. In one series the initial product of the condensation was reduced promptly, before secondary changes could much interfere; this procedure led in every case to ***N-methylation,*** yielding tertiary bases. In the other series the amines were condensed with formaldehyde in dilute hydrochloric acid solution, and the solid hydrochlorides of the resulting bases allowed to precipitate. They were isolated, analyzed and submitted to vigorous reduction; in every case the corresponding alkyl-*p*-toluidine was obtained in quantity, the net result being ***nuclear*** *methylation*

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(8) German Patent 96,851; *Friedl* , 5, 91.

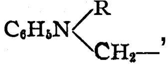
(9) Green and Saunders, J *Soc. Dyers and Colourists*, *29*, 10 (1923).

(10) Goldschmidt, *Chem.-Ztg.*, 24, 284 (1900); 26, 606, 967 (1902); German Patent 97,710

(11) Friedlander, *Monatsh* , 23, 973 (1902).

(12) German Patent 376,013 (1920); 491.856 (1923). 503,113 (1924)

(13) V Braun and co-workers, *Ann*, 472, 1 (1929).

of the original amine. These results confirm the opinion that condensation in acid solution involves initially the nitrogen atom, yielding a compound which contains the unit  $C_6H_5N{<}\begin{matrix}R\\ CH_2-\end{matrix}$, and they show the separated hydrochlorides to have the same essential structure as Friedländer's dimeric anhydro-*p*-methylaminobenzyl alcohol, *i. e.*, to contain the unit  $\underset{|}{R}NC_6H_4\underset{|}{C}H_2$, which clearly is obtained from the first by a secondary rearrangement or condensation.

Experimental

General.—The alkylanilines used were Kahlbaum or Eastman products. In the analyses reported below, nitrogen was determined by the Kjeldahl method, using the boric acid modification, with methyl red as indicator, and halogen was determined by the sodium peroxide bomb method, the silver halide being weighed. Melting points were determined in an apparatus of the Anthes type,[14] provided with a mechanical stirrer in the bulb, and with the elongated neck vacuum-jacketed to permit more accurate stem corrections. Boiling points were determined in a small side-arm flask, using short-scale thermometers, the apparatus being that recommended by Mulliken.[15] Boiling points stated are substantially "corrected," though with several of the higher-boiling bases the entire mercury column, while within the flask, was not completely immersed in the vapors. All thermometers used had been calibrated.

N-Methylations of Alkylanilines by Reduction of the Initial Condensation Products with Formaldehyde in Acid Solution.—The procedure for methyl-, ethyl-, propyl- and butylanilines was as follows. The base was dissolved in dilute hydrochloric acid, the solution cooled to 20° or below in an ice-bath, and slightly more than one equivalent of formaldehyde added as a 35% solution. Within five minutes an excess of zinc dust was introduced as rapidly as possible without causing the temperature to exceed 25°, the mixture being vigorously stirred mechanically; more hydrochloric acid was added at intervals to maintain a brisk action. In a typical experiment there were used 15 g. of methylaniline dissolved in 75 cc of water and 20 cc. of concd. hydrochloric acid; the chilled solution was treated with 12 cc. of 35% formaldehyde, 25 g. of zinc dust added and 80 cc. of concd. hydrochloric acid introduced gradually, the temperature being kept around 25°. The liquid was finally colorless and clear except for some undissolved metal.

With isoamylaniline the above procedure yielded an intermediate semi-solid material which trapped the zinc dust. To effect reduction it was necessary to raise the temperature to 70° or above, and to make further additions of zinc and acid. The liquid was finally clear, and the yield of methylisoamylaniline fairly good

The reduction liquid was made alkaline with sodium hydroxide and the dialkylaniline distilled out with steam, extracted in ether, dried with sodium sulfate, the extract filtered and the product obtained by evaporation of the ether; it was purified by careful redistillation and then identified. The tertiary bases made in this way were all of good quality, boiling when crude within ranges of 4–5°, readily narrowed to 1–2° upon redistillation. The best yields varied, for the several amines, from 55 to 88%. There seemed to be no secondary amine finally present, indicating that the condensa-

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(14) Houben, "Die Methoden der organischen Chemie," Geo. Thieme, Leipzig, Vol. I, 3d ed , 1925, p. 798.

(15) Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. I, 1904, p. 221.

tions with formaldehyde were rapid and complete. In experiments conducted at higher temperatures there was increased formation of material not volatile with steam, shown in one case to be the *p,p'*-bis-(dialkylamino)-diphenylmethane.

Data for individual experiments are given in Table I.

TABLE I

REDUCTION OF THE INITIAL CONDENSATION PRODUCTS OF SOME ALKYLANILINES WITH FORMALDEHYDE IN ACID SOLUTION

Product, dialkyl-aniline	Best yield crude, %	B. p. redist., °C.	Identification		
			Nitrogen, %		
			Found	Calcd.	Derivative
Dimethyl	79.6	194–195	...	...	*p*-Nitroso compound, m. p. 87°
Methylethyl	87.8	207–209"	10.17	10.37	Picrate,[b] m. p. 129–129.5°
Methyl-n-propyl	75.5	222–224	9.42	9.39	Picrate,[c] m. p. 110.5°. Hydrochloride, see below
Methyl-n-butyl	54.9	241–242.4	...	...	Note[d]
Methylisoamyl	60.5	253–255[e]	7.75	7.91	Picrate,[f] m. p. 89.5"

[a] This value probably better than the b. p. 201° reported by Claus and Howitz [*Ber.*, 17, 1325 (1884)] for methylethylaniline not specially purified.

[b] Komatsu [*Mem. Coll. Sci.* Eng. *Kyoto Imp. Univ.*, *3*, 371 (1912); *Chem. Abstracts*, 7, 1021 (1913)] reported the value 121–122°. A number of Komatsu's constants are incorrect; see Reilly and Hickinbottom, note *d*, and also notes c and f.

[c] Meisenheimer [Ann., 449, 196 (1926)] reported 109°; Komatsu's value was 103–104°.

[d] Boiling point in good agreement with value 242.5" reported for the pure base by Reilly and Hickinbottom [*J. Chem. Soc.*, 117, 109 (1920)].

[e] Previous values, for speamens made by two distinct methods and not specially purified: 257° (Claus and Rautenberg) and 246–248° (Thomas and Jones).

[f] This picrate separated as oil from ordinary or aqueous alcohol, but crystallized from hot absolute alcohol. Komatsu reported m. p. 93–94°.

In the first preparation of dimethylaoiline (Table I), using higher temperature (70–75°) for condensation and reduction, the main product was a solid not volatile with steam. It was crystallized several times from alcohol, and the melting point thus raised from 72 to 82°, with indications that the substance was still impure. It was eventually identified as *p,p'*-bis-(dimethylamino)-diphenylmethane by means of the picrate, which melted at 178°, and by its nitrogen content of 11.05% (calcd., 10.90%). A mixed melting point test of the picrate with a specimen (m. p. 179° corr.), made from the base prepared in the usual way, gave the result 178.5° corr.. and confirmed the identification.

As an additional identifying derivative for methyl-n-propylaniline the hydrochloride was prepared (in dry ether). It melted 120–122° uncorr., and analyzed satisfactorily: nitrogen, 7.47% (calcd., 7.55%), chlorine, 18.84% (calcd. 19.11%) The melting point 106°, reported by Claus and Hirzel[16] for an impure specimen prepared from an impure base (b. p. 212") is therefore incorrect.

In the preparation of methylisoamylaniline there was formed an oily product not volatile with steam. This was distilled in *vacuo*, and after three distillations yielded a main fraction boiling at 275–280" at 10 mm. (282–287° corr.). Analysis for nitrogen gave 7.50, 7.51%, indicating the compound to be probably *p,p'*-bis-(methylisoamylamino)-diphenylmethane (nitrogen, calcd., 7.65%), formed by side reaction during the hot reduction.

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[16] Claus and Hirzel, *Ber.*, 19, 2785 (1886).

Nuclear Methylations of Alkylanilines by Reduction of the Anhydro-*p*-alkylaminobenzyl Alcohol Salts

(a) Preparation of the Anhydro-*p*-alkylaminobenzyl Alcohol Salts.—The conditions approximated those given in references previously cited[10,11] The amine was dissolved in four to five parts of water by addition of slightly more than one equivalent of hydrochloric acid. The solution was chilled in ice, and treated with a small excess of formaldehyde, added as a 35% solution. After about an hour the mixture was allowed to come to room temperature, when there separated after a time the solid amine salt, the liquid generally "setting" The product was filtered off the following day, and the filtrate allowed to stand a further time. from one to several smaller crops of product being thus frequently obtained. The salt was washed with cold water containing hydrochloric acid. The methyl, ethyl and propyl compounds were highly crystalline and white. They were washed finally with alcohol, then with ether and were dried in *vacuo.* The butyl and amyl compounds were yellowish and granular. Attempted washing with alcohol rendered them slimy and unfilterable, so these compounds were dried thoroughly in *vacuo* after washing with water containing hydrochloric acid.

The methyl, ethyl and propyl compounds are soluble in water, and are reprecipitated by addition of hydrochloric acid; the corresponding bases are precipitated by alkali or sodium acetate. The butyl and amyl compounds are not appreciably soluble in water. All five compounds dissolve in dilute sulfuric acid. The n-propyl, n-butyl, and isoamyl compounds appear to be new. Yields and analytical data are given in Table II.

TABLE II

PREPARATION OF SOME ANHYDRO-*p*-ALKYLAMINOBENZYL ALCOHOL SALTS

Product $\mathrm{RNC_6H_4CH_2(HCl)}$ R =	Best yield, %	Nitrogen, % Found	Nitrogen, % Calcd [a]	Chlorine, % Found	Chlorine, % Calcd [a]	No. of specimens anal
Methyl	83.4	8.54	9.01	21.96	22.80	4
Methyl (hydrobromide[b])	86	6.85	7.01	38.70	39.96	1
Ethyl	76.5	8.15	8 26	20.71	20.91	2
n-Propyl	57	7.52	7.63	19.18	19.32	2
n-Butyl	90.6	6.53	7.09	18.30	17.95	2
Isoamyl	96.4	6.26	6.62	1587	16.76	3

[a] Yields and elementary percentages are calculated from the formula at the head of the first column.

[b] Prepared from methylaniline, formaldehyde and hydrobromic acid; *cf.* Goldschmidt *Chem.-Ztg.*, 26, 967 (1902).

For the ethyl and n-propyl compounds (Table II) the analytical results support the formula $\mathrm{CH_2C_6H_4NR(HCl)}$. For the methyl compound Friedlander's results could not be duplicated.[17] The averaged values for four specimens indicate a molecular weight of 161.6 per atom of chlorine, or 164.2 per atom of nitrogen, *i.* e., 6 and 8.6 units higher than required by formula, and suggest possible presence of a molecule of water for each dimeric molecule of the salt. The butyl and isoamyl compounds likewise yielded results for nitrogen and chlorine lower than those required by formula, but these compounds were probably less pure than the first three. All these compounds, however, were reproducible within rather narrow limits of composition and their identity in essential structure was shown by their reducibility to the corresponding alkyl-p-toluidines.

There was a noticeable delay in the precipitation of these salts. Their separation

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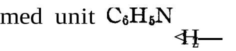
[17] Friedlander determined only chlorine (by direct precipitation with silver nitrate from aqueous solution acidified with nitric acid) and obtained 22.74%.

was much retarded if the reaction mixture was kept cold. At room temperature precipitation usually began only after an hour or more, and in some cases continued for days. As was shown by the experiments on N-methylation above, the condensation of amine and formaldehyde is rapid; further, the anhydro-*p*-alkylaminobenzyl alcohol hydrochlorides when dissolved in water are promptly precipitated by hydrochloric acid. It is therefore obvious that the delay noticed in every case was not due to a slow amine-aldehyde condensation, nor to a lag in precipitation of the amine-salt, but that it represented the interval during which there occurred the secondary change by which the first-formed unit  $C_6H_5N\underset{\text{<H}_2\text{—}}{}$ assumed the structure —$CH_2C_6H_4NR$—. It seems that a kinetic study of one of these reactions should be feasible.

(b) Reduction of **Anhydro-*p*-alkylaminobenzyl** Alcohol Salts to **Alkyl-*p*-toluidines.**—Reduction was most successful using zinc dust and dilute sulfuric acid at 70–85°. Cold reduction was ineffective, and hydrochloric acid was unsatisfactory because of its salting-out action. For the reductions two procedures were used. (1) The methyl, ethyl and propyl compounds were dissolved or suspended in 10–20 parts of 3 *N* sulfuric acid, the mixture stirred mechanically, some zinc dust added, and the temperature raised quickly to 70–85°. As rapidly as possible the rest of the zinc dust (in all about twice the weight of the compound to be reduced) was added, and the reduction temperature was maintained, with vigorous stirring, until action ceased. (2) The butyl and isoamyl compounds were ground with twice their weight of zinc dust, and the mixture added in small portions, but rapidly, to the hot acid. In either case reduction was rapid, with usually not more than moderate frothing, and the liquid was finally colorless and clear except for some undissolved metal. It was found advisable to reduce not more than 5 or 10 g. of the anhydro-alkylaminobenzyl alcohol salts at a time, the operations outlined then requiring about thirty minutes.

The reduction liquid was made alkaline with sodium hydroxide and was steam-distilled until no more oil passed over. The oil was extracted in ether, the solution dried with sodium sulfate and filtered, and the product obtained as a residue or by distillation after removal of the ether. The best yields of the alkyl-*p*-toluidines ranged from 54 to 80%. The products, as obtained by steam distillation, seemed to be substantially pure, boiling within narrow ranges; on redistillation the widest boiling range observed for any main fraction was 1.5". The alkyl-*p*-toluidines were fully identified; isoamyl-*p*-toluidine has apparently not been prepared hitherto

In all these experiments there remained in the steam distilling flask an oil not volatile with steam. This was examined in several cases and found to consist largely of the corresponding *p,p'*-bis-(alkylamino)-diphenylmethane.

In preliminary experiments it was found that anhydro-*p*-methylaminobenzyl alcohol was not hydrolyzed under the conditions of reduction, no steam volatile product resulting. The anhydromethylaminobenzyl alcohol itself was found to be non-volatile with steam. The steam volatile oils obtained by reduction of the methyl and ethyl compounds were examined for primary ortertiary amines, but no such products could be isolated, nor was there any indication that some of the original alkylaniline contaminated the alkyl-*p*-toluidine.

Data as to yields and identification of products obtained in these reductions are given in Table III.

In the first preparation of methyl-*p*-toluidine (Table III) the oil not volatile with steam was distilled *in vacuo*, and identified as *p,p'*-bis-(methylamino)-diphenylmethane. It yielded a nitrosamine of m. p. 97–97.5' uncorr., identical with a specimen (m. p. 97–98" corr.)[18] made from the base prepared as described by v. Braun,[19] as shown by

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[18] V. Braun and Kayser, *Ber.*, 37, 2675 (1904).

[19] V. Braun, *ibid.*, 41, 2148 (1908).

TABLE III

REDUCTION OF ANHYDRO-*p*-ALKYLAMINOBENZYL ALCOHOL SALTS TO ALKYL-*p*-TOLUIDINES

Product,[a] alkyl-*p*-toluidine	Best yield[b] crude, %	B. p. redist., °C.	Identification				
				Nitrogen, %		Chlorine, %	
			Compound	Found	Calcd.	Found	Calcd.
Methyl	53.6	212–212.9	Benzenesulfonyl deriv., m. p. 65°[c]	..	..	...	...
Ethyl	70.6	222	Benzenesulfonyl deriv., m. p. 57°[c]	..	..	...	...
			Picrate[d] m. p. 139.6°	..	..	...	...
n-Propyl	79.6	237.3–238.8	Base	9.38	9.39	...	...
			Hydrochloride, m. p. 155°	7.45	7.55	18.90	19.11
n-Butyl	55.7	255–256	Base	8.47	8.59	...	...
			Hydrochloride, m. p. 148–149°	6.90	7.02	17.63	17.76
Isoamyl	56.9	267–268	Base	7.77	7.91	...	...
			Hydrochloride, m. p. 146°; from dil. HCl	6.52	6.56	16.69	16.60

[a] In every case the material reduced was the corresponding anhydro-*p*-alkylaminobenzyl alcohol salt.

[b] Yields are calculated from the ideal formulas for the salts, and for the methyl, butyl and amyl compounds are therefore slightly lower than if based upon analysis (Table II).

[c] Identification verified by mixed melting point test with the same derivative prepared from Eastman Co. alkyl-p-toluidine.

[d] The picrate obtained from Eastman Co. ethyl-p-toluidine melted at 140°.

[e] Reilly and Hickinbottom [J. Chem. *Soc.*, 113, 977 (1918)] found the boiling point of carefully purified *n*-butyl-*p*-toluidine to be 264–265° (766 mm.).

mixed melting point test. The preparation of ethyl-*p*-toluidine yielded a similar by-product, whose nitrosamine (from alcohol and ether) melted at 81° uncorr., close to the value (83°) found by v. Braun[20] for the nitrosamine of *p,p'*-bis-(ethylamino)-diphenylmethane.

Summary

1. The secondary aromatic amines methyl-, ethyl-, n-propyl-, *n*-butyl- and isoamylanilines, when condensed with formaldehyde in aqueous solution in presence of hydrochloric acid, yield solid products which have, or approximate, the composition $[\mathrm{R\underset{|}{N}C_6H_4\underset{|}{C}H_2(HCl)}]_n$, and are to be considered the hydrochlorides of the anhydro-*p*-alkylaminobenzyl alcohols. This essential structure was shown by reduction of these compounds to the corresponding alkyl-*p*-toluidines.

2. When the same secondary amines are condensed with formaldehyde in acid solution, with prompt reduction of the initial condensation product, they are methylated to yield the corresponding tertiary amines.

3. It is concluded that condensation of these monoalkylanilines with formaldehyde in acid solution involves primarily the nitrogen atom, and

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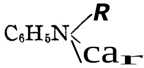
[20] V. Braun, Ref. 19, p. 2151.

yields first a compound which contains the unit  $C_6H_5N{<}^{R}_{CH_2-}$, reducible to methylalkylaniline. The formation of the anhydro-*p*-alkylaminobenzyl alcohol salts, which eventually occurs under the same conditions but in absence of reducing agent, is therefore not the result of a special primary condensation, but of a secondary intra- or intermolecular action, probably a coupling of the units shown in (1).

4. By the procedures described either nuclear or N-methylation of alkylanilines can be effected by means of formaldehyde.

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Alkyl-Nitroguanidines. Dearrangement and Preparation by Nitration[1]

BY TENNEY L. DAVIS AND ROBERT C. ELDERFIELD

Nitroguanidine dearranges in two modes and may be used for synthesis in two ways by taking advantage of the products which result from its dearrangement in one manner or the other. Thus, with ammonium carbonate it yields guanidine carbonate, and with primary aliphatic amines it gives N-alkyl-N′-nitroguanidines.[2] These alkyl-nitroguanidines, having a hydrogen atom attached to each of the guanidine nitrogens, are capable of dearrangement in two modes, as follows.

$$\text{RNH—C(NH)—NH—NO}_2 \rightleftharpoons \begin{cases} \text{RNH}_2 + \text{HNCN—NO}_2 & \text{(I)} \\ \text{RNCNH (or RNHCN)} + \text{NH}_2\text{—NO}_2 & \text{(II)} \end{cases}$$

The first of these modes corresponds to the method by which the substances have been synthesized from nitroguanidine; the second opens new possibilities of synthesis. We have therefore wished to determine whether the alkyl-nitroguanidines dearrange in the predicted manner and to investigate their usefulness for the easy preparation of monoalkyl- and N,N′-dialkyl-guanidines by reaction with ammonia and with primary amines, respectively.[3]

As no alkyl-nitroguanidines have heretofore been prepared by the nitration of alkyl-guanidines, we have studied that reaction in an effort to gain a further insight into the mechanism of the nitration of amines, and have found that the only alkyl-nitroguanidines which we have been able to

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(1) A summary of part of the Doctor's Dissertation of Robert C. Elderfield, Massachusetts Institute of Technology, June, 1930.

(2) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, 61, 437 (1928); Davis and Luce, THIS JOURNAL, 49, 2303 (1927).

(3) Other papers on the urea dearrangement: Davis and Underwood, *ibid.*, 44, 2595 (1922); Davis and Blanchard, *ibid.*, 45, 1816 (1923); Davis, *Proc. Nat. Acad. Sci.*, 11, 68 (1925); Davis and Blanchard, THIS JOURNAL, 51, 1790, 1801, 1806 (1929).

produce by this method are identical with those resulting from the other method of synthesis. The relation of this finding to the question of the basicity of the substituted guanidines is discussed.

Dearrangement of the **N-Alkyl-N'-nitroguanidines** and its Application in Synthesis.—When methyl-nitroguanidine was refluxed with water, it decomposed slowly into gaseous products, methylamine carbonate collected in the condenser, and the solution, after one hundred hours of boiling, yielded no residue on evaporation to dryness. No cyanic acid could be detected in the solution, and no trimethylisomelamine, from the polymerization of methylcyanamide, could be isolated. The facts agree with the belief that dearrangement under these conditions occurred according to the second of the above-indicated modes. If the dearrangement had produced methylamine and nitrocyanamide, then the nitrocyanamide, decomposing in the manner usual with nitroamines, would have formed nitrous oxide and cyanic acid, the cyanic acid would have combined with the methylamine and methylurea would have been found when the solution was evaporated to dryness. If the dearrangement produced methylcyanamide and nitroamide, the nitroamide would have decomposed into nitrous oxide and water, and the methylcyanamide, being extremely stable to polymerization in neutral solution, would have hydrolyzed slowly to methylamine, ammonia and carbon dioxide. In other experiments we have found positive proof of the presence of the alkylcyanamide, both by the production from it of mono- and dialkyl-guanidines and by the isolation of the trialkylmelamine.

When the alkyl-nitroguanidines were warmed with water and a large excess of ammonium carbonate, nitrous oxide was liberated and unsubstituted guanidine carbonate was the principal product. Dearrangement occurred in the first mode corresponding to the process by which the alkylnitroguanidine was produced in the first place from nitroguanidine, nitroguanidine was formed and dearranged in its turn to give nitroamide, which decomposed, and cyanamide which combined with the ammonia to form guanidine as has been demonstrated earlier. Methyl-, n-butyl- and benzyl-nitroguanidine thus yielded guanidine carbonate in 72–74% of the theoretical amount. In the experiment with n-butyl-nitroguanidine, a small amount of n-butylguanidine (4.2%) was isolated, indicating that dearrangement in the second mode took place to a small extent.

When the alkyl-nitroguanidines were refluxed in water solution with the corresponding primary amine, nitrous oxide came off, and, instead of the expected dialkylguanidine, about 70% of the theoretical amount of the monoalkylurea was obtained. In some experiments, however, a certain quantity of the dialkylguanidine was isolated. At first sight the production of the mono-substituted urea seems explainable in two ways. Either dearrangement took place in the first mode, and the nitrocyanamide lost nitrous oxide to form cyanic acid which combined with the amine to produce the substituted urea; or, the dearrangement being in the second mode, the alkylcyanamide was hydrolyzed to the alkylurea by the action of the basts which were present. An experiment with N,N-dimethyl-N'-nitroguanidine cast doubt upon the first explanation. This substance can dearrange in only one manner, namely, into dimethylamine and nitrocyanamide. After refluxing for twelve hours with a water–alcohol solution of an excess of trimethylamine (chosen because it supplied alkalinity and would form a cyanate but not a urea derivative), 92% of it was recovered unchanged, no allophanic ester was found, and the solution gave no test for cyanate. The second explanation is supported by the fact that a decrease in the alkalinity of the reaction mixture leads to a decrease in the amount of alkylurea which is formed and to an increase in the amount of dialkylguanidine.

Cyanamide itself combines with water readily, especially in alkaline solution, to produce urea. Hetherington and Braham[4] have studied the polymerization and hydrolysis of cyanamide in 0.01, **0.1** and **1.0** molal solutions of sodium hydroxide, and have found that urea is formed as well as dicyandiamide, increased alkalinity resulting in increased urea formation. Buchanan and Barsky[5] in an exhaustive and careful study have confirmed these results; cyanamide polymerizes to dicyandiamide in moderately alkaline solutions, but in strongly alkaline solutions it is entirely hydrolyzed to urea. Since the alkylcyanamides are not known to form dimers corresponding to dicyandiamide, they would be expected—as we have found to be the case—to polymerize to trialkylisomelamines in solutions which are not strongly alkaline enough to hydrolyze them to urea derivatives. Two sources of alkalinity existed in our experiments; the reaction mixtures were about three molal. in amine at the start, and the dialkylguanidines which are produced are strong bases, as we have reported,[6] and increased the alkalinity as the reaction progressed, thus militating against their further formation.

Experiments were tried in which the alkalinity of the reaction mixtures was reduced by the addition of varying amounts of acetic acid. The increased hydrogen-ion concentration had the effect of inhibiting the dearrangement, and it was necessary to heat the materials in sealed tubes at 175°. The primary amine, reacting with the alkyl-nitroguanidine, gave the best yields of N,N'-dialkylguanidine (about 40 to about 50% according to the alkyl group) when the *P*H at the beginning of the experiment was about **6.13.** This PH also corresponded to the lowest yields of the urea derivative. In more alkaline solutions the yields of the urea derivative were greater because of increased hydrolysis of the alkylcyanamide. In

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(4) Hetherington and Braham, THIS JOURNAL, **45**, 828 (1923).

(5) Buchanan and Barsky, *ibid.*, 62, 195 (1930)

(6) Davis and Elderfield, *ibid.*, 64, 1499 (1932).

more acid solutions they were greater because, as we believe. the increased acidity inhibited the addition of the amine to the alkylcyanamide and so left the latter material available only for polymerization or for hydrolysis by the hot solution. We expect in the future to investigate more fully the conditions which influence the combination of a cyanamide with an ammonia derivative. In these sealed tube experiments, the products of the hydrolysis of the alkylcyanamides were isolated in the form of N,N'-dialkylureas, as would be expected, for the mono-substituted ureas, by dearrangement, would change over to these substances at the high temperature which was used.

When the alkyl-nitroguanidines were made to react in water solution with the corresponding amines by refluxing under a pressure (above atmospheric pressure) of 508 cm. of mercury while carbon dioxide was bubbled through the liquid, about 40% of the material was obtained in the form of N,N'-dialkylguanidine and about 40% in the form of trialkylisomelamine. The carbon dioxide reduced the alkalinity enough to prevent any considerable hydrolysis of the alkylcyanamide resulting from the dearrangement and, in the less strongly heated solution, created a condition favorable for the polymerization of that portion of the substance which did not combine with the amine.

The dearrangement of the alkyl-nitroguanidines to form alkylcyanamide and nitroamide appears to be fully demonstrated by the isolation of the polymer of the alkylcyanamide and of the several substances which correspond to the interaction of the alkylcyanamide with water, with ammonia and with amines, respectively, by the evolution of nitrous oxide from the reaction mixtures, and by the fact, previously reported, that the alkyl-nitroguanidines give up their nitro group nitrogen quantitatively in the nitrometer. The conditions which promote the dearrangement are clearly not the conditions which most promote the addition of ammonia or of amines to the alkylcyanamide and at the same time most reduce the tendency of the alkylcyanamide to enter into the side reactions of hydrolysis and polymerization. We conclude that the dearrangement of the alkyl-nitroguanidines does not supply the best method for the synthesis of substituted guanidines.

The results however have another interest. They show that the mechanism of the hydrolysis of the alkyl-nitroguanidines is first dearrangement and then hydrolysis of the dearrangement products. The hydrolysis cannot be the replacement of the NH group by an oxygen atom with the formation of an alkyl-nitrourea, as would be expected if one accepts the conclusions of Bell,[7] who supposes that the production of urea from guanidine, under the conditions where this "hydrolysis" occurs, is due to the hydrolysis of the guanidine molecule as a whole. We believe, on the

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(7) Bell, *J. Chem. Soc.*, London, 118, 1213 (1926); 120, 2074 (1928).

contrary, that the urea results from the hydrolysis of the cyanamide produced by the dearrangement of the guanidine—just as in our experiments, where the alkyl group serves as a label or marker for the nitrogen atom to which it is attached, the alkylurea is certainly produced by the hydrolysis of the alkylcyanamide.

Nitration of Alkylguanidines.—In guanidine salts the acid is possibly combined with one of the amino nitrogen atoms (or amino groups) in the same way, whatever that way may be, that hydrochloric acid, say, is combined with the ammonia nitrogen atom (or the ammonia molecule) in ammonium chloride. There is also the possibility that the acid may be combined in some manner with the guanidine molecule as a whole. The introduction of an alkyl group into ammonia increases its basicity, and the introduction of an alkyl group into guanidine would be expected to increase the basicity of the nitrogen atom to which it is attached and hence to impart greater basicity to the molecule as a whole. In a salt of such an alkylguanidine, it would be expected that the acid would be in combination with the alkylated nitrogen atom or amino group. If, now, the salt being a nitrate, an alkyl-nitroguanidine is formed from it by a process of dehydration, the nitro group in the resulting compound would be attached to the nitrogen atom to which the nitric acid of the nitrate was previously attached, that is, to the nitrogen which carries the alkyl group.

We have found that the nitrates of methyl-, *n*-butyl-, n-heptyl- and N,N-dimethylguanidine, when treated with concentrated sulfuric acid, yielded alkyl-nitroguanidines identical with those already known in which the nitro group is attached to *a* different nitrogen atom from that which carries the alkyl group or groups. If the nitro compound is produced by a process of dehydration, then the nitric acid in the nitrate was not attached to the alkylated amino group. If the nitrate reacts with the sulfuric acid to produce nitric acid which then nitrates the substance, then the nitric acid in the original nitrate may have been attached to the base in any manner whatever, whether to the alkylated or the non-alkylated amino group or to the molecule as a whole.

Benzylguanidine nitrate carbonized on treatment with concentrated sulfuric acid producing sulfur dioxide; piperidylguanidine nitrate gave a yellow solution and some sulfur dioxide, and neither substance yielded a nitro compound. The nitrates of N,N′-dimethyl- and N,N′,N″-trimethylguanidine dissolved in sulfuric acid to yield solutions from which no nitro compound could be isolated and from which the bases (87%) were recovered in the form of picrates.

Methyl-, n-butyl- and N,N-dimethylguanidine sulfate, on treatment with concentrated sulfuric acid and potassium nitrate, nitrated in the unsubstituted amino group as before, but now under conditions in which it is difficult to believe that the formation of the nitro compound was due to a process of dehydration. In a similar experiment with the sulfate of N,N'-diethylguanidine, and in an attempt to nitrate N,N',N"-trimethylguanidine with mixed acid, no nitro compound could be isolated and the bases were recovered in large part in the form of their picrates. We conclude that only those alkylguanidines which contain an unsubstituted amino group form nitro compounds by direct nitration, the nitro group entering the non-alkylated amino group.

Since it seems less likely that the acid in the guanidine salt is attached to the unalkylated amino group than to the more basic alkylated one, and in view of the nitrations which have been accomplished without the preliminary preparation of the nitrate, we conclude that the mechanism of the nitration is probably not dehydration. To test the matter further we have treated guanidine nitrate with a mixture of phosphoric acid and phosphorus pentoxide, a mixture which ought to be as strong and as prompt a dehydrating agent as concentrated sulfuric acid, and have recovered over 95% of the guanidine after thirty minutes heating at 65° and after thirty hours standing at room temperature. After forty-eight hours at room temperature, during which time nitric acid or nitrophosphoric acid was doubtless produced, an 82% yield of nitroguanidine was secured.

If the basicity of guanidine is a property of one of the nitrogen atoms (or amino groups) rather than of the molecule as a whole, then the introduction of alkyl groups would be expected to increase the basicity of the substance, or certainly not to reduce it.[6] We have found that the monoalkylguanidines (which form nitro compounds) are as strong bases as guanidine itself, but that the N,N'-dialkylguanidines (which do not nitrate) are markedly weaker. The facts so far can be explained on the unlikely supposition, suggested above, that the strong basicity of guanidine and its monoalkyl derivatives is resident in the unsubstituted NH_2 group (where nitration occurs). But that supposition is contradicted by the fact that N,N',N^n-trimethylguanidine (which does not nitrate) is again as strong a base as guanidine. The facts altogether suggest that the acid in guanidine salts is not attached to any particular part of the molecule but is attached to the molecule as a whole.

Experiments

Experiments which are indicated with sufficient fullness in the foregoing are not again described in this section. Experiments are reported in the order in which their results are discussed in the first section of the paper.

Methyl-nitroguanidine and Ammonium Carbonate.—Ten grams of methyl-nitroguanidine. 350 g. of ammonium carbonate. and 200 cc. of water were warmed together under reflux in the water-bath at 65–70° for five hours until everything had gone into solution. The liquid was evaporated to dryness, and the residue, after twice dissolving in water and precipitating with alcohol, yielded pure guanidine carbonate, 72% of the theoretical amount, identified by its melting point and by the melting points of the picrate, nitrate and nitro compound prepared from it.

n-Butyl-nitroguanidine and Ammonium Carbonate.—A mixture of 20 g. of n-butyl-nitroguanidine, 500 g. of ammonium carbonate and 500 cc. of water required about seven hours of heating at 65–70" before all of the n-butyl-nitroguanidine went into solution. Precipitation by alcohol yielded 8.31 g. of guanidine carbonate, 74%. The liquor from the precipitation yielded a gummy mass on evaporation, and this, on treatment with ammonium picrate, gave 2.1 g. of a crystalline picrate. Four recrystallizations from 20% alcohol gave the pure substance, bright yellow needles, melting sharply at 154.5° and identified as butylguanidine picrate by analysis.[8]

Methyl-nitroguanidine and Methylamine.—Ten grams of methyl-nitroguanidine, 9 g. of a 33% methylamine solution, and 50 cc. of water were refluxed together on the boiling water-bath for three hours. A constant slow evolution of nitrous oxide took place. Evaporation gave a thick sirup which yielded 8.00 g. of crystals upon treatment with dilute nitric acid. These, recrystallized from water, melted at 127–128° with slight decomposition, in agreement with the melting point of methylurea nitrate reported by Franchimont.[9] The nitrate, evaporated with a solution of an equivalent amount of potassium carbonate and worked up from acetone, yielded methylurea, m. p. 101°, identified by mixed melting point with a known sample. The yield of methylurea amounted to 69%.

Ethyl-nitroguanidine and Ethylamine.—A mixture of 13.2 g. of ethyl-nitroguanidine, 15 g. of a 33% solution of ethylamine, and 50 cc. of water, after refluxing for three hours, was evaporated to a thick sirup which deposited 6.38 g. of crystals after standing for several days, m. p. 92° after recrystallization from acetone, identified as ethylurea by mixed melting point with a known sample; yield, 72.5%.

n-Butyl-nitroguanidine and n-Butylamine.—Ten grams of n-butyl-nitroguanidine, 9 g. of n-butylamine and 30 cc. of water were heated together under reflux for five hours in a water-bath at 80° and for three hours in a boiling water-bath. Evaporation yielded a thick sirup which would not crystallize. Taken up in water and treated with an ammonium picrate solution, it gave 3.2 g. of a picrate, m. p. 122.5" after recrystallization from dilute alcohol.

Anal. Calcd. for di-n-butylguanidine picrate: N, 21.00. Found: N, 21.59, 21.35, 21.29. Yield of di-n-butylguanidine, 12.80%. The oil remaining from the picrate precipitation could not be made to crystallize or to yield any precipitate with a variety of reagents.

Effect of Hydrogen-Ion Concentration on the Reaction of an Amine with an Alkyl-nitroguanidine.—Approximately 3 N solutions of the amines were made up and their exact strengths were determined by titration with standard acid. To portions of these solutions acetic acid was added in such amounts that the ratios of acetic acid to amine were known, and the hydrogen-ion concentrations of the mixtures were determined electrometrically. Weighed portions of the alkylnitroguanidines were heated in sealed tubes at 175° for eight hours with quantities of the various solutions which contained in every case 1.1 molecular equivalents of the corresponding amine. After the heating the tubes contained considerable gas under pressure.

In the experiments with n-butylamine and n-butyl-nitroguanidine, no attempt was made to obtain dibutylurea because of the difficulties attendant upon the quantitative estimation of that substance. The contents of the sealed tubes were washed out, and the dibutylguanidine was precipitated as picrate, which was collected, washed, dried, weighed, recrystallized from benzene and identified by mixed melting point with a known sample.

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(8) Analyses of nearly all the sulfates, nitrates and picrates which are mentioned in this paper have been reported in an earlier article.[6]

(9) Franchimont, Rec. *trav. chim. Pays-bas.*, 3, 220 (1884).

In the experiments with *n*-amylamine and n-amyl-nitroguanidine, the contents of the sealed tubes were washed onto filters, the solid matter was washed with cold water until the washings gave no precipitate with ammonium picrate, and the diamylurea which remained was dried, weighed, recrystallized from water, and identified by mixed melting point, 92.8°, with a known sample. The filtrates were precipitated with ammonium picrate, and the precipitates collected, etc., and recrystallized from benzene to constancy of melting point at 108°.

In the experiments with the n-heptyl derivatives, the reaction mixture was worked up in the same manner. The di-n-heptylurea, after recrystallization from dilute alcohol, melted at 91° as reported by Manuelli and Ricca-Rosellini,[10] and its melting point was not lowered by mixture with a sample, m. p. 91°, prepared from nitrourea and n-heptylamine. The di-n-heptylguanidine picrate, after recrystallization from alcohol, melted at 278° with decomposition.

Anal. Calcd. for di-n-heptylguanidine picrate: N, 17.35. Found: N, 17.21, 17.51.

In the experiments with the benzyl derivatives, the dibenzylguanidine could not be determined as picrate for the reason that benzylamine picrate precipitated at the same time and could not be separated from it. The dibenzylurea was collected by filtering the reaction mixture, recrystallized from dilute alcohol, and identified by mixed melting point with a known sample.

The results of the series of experiments are summarized in Table I

TABLE I

EFFECT OF HYDROGEN-ION CONCENTRATION ON THE PRODUCTS OF THE REACTION OF A PRIMARY AMINE WITH THE CORRESPONDING ALKYLNITROGUANIDINE

Alkyl	Ratio of acetic acid to amine	P_H	Yield, % Dialkylurea	Yield, % Dialkylguanidine
n-Butyl	1.1	5.34	..	13.5
n-Butyl	1.0	5.59	..	32.6
n-Butyl	0.9	6.13	..	38.2
n-Butyl	0.8	9.51	..	17.6
n-Amyl	1.1	5.67	37.1	16.0
n-Amyl	1.0	6.13	28.1	47.0
n-Amyl	0.9	9.46	33.0	42.1
n-Amyl	0.8	9.90	45.3	32.9
n-Heptyl	1.1	5.63	39.5	41.4
n-Heptyl	1.0	6.12	20.5	52.8
n-Heptyl	0.9	8.61	49.0	37.2
n-Heptyl	0.8	9.07	53.9	21.2
Benzyl	1.1	6.06	8.2	..
Benzyl	1.0	7.96	11.1	..
Benzyl	0.9	8.56	13.1	..
Benzyl	0.8	8.84	15.1	..

Effect of Carbon Dioxide.—Ten grams of methyl-nitroguanidine and 150 cc. of 21% methylamine solution were refluxed together under a pressure (above atmospheric pressure) of 508 cm. of mercury while carbon dioxide was bubbled through the solution. At the end of ten hours all of the methyl-nitroguanidine had disappeared and the solution no longer gave a blue color when a test portion was treated with a solution of diphenylamine in concentrated sulfuric acid. The reaction mixture, evaporated to a small volume and chilled, gave a white solid which, after recrystallization from a little

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(10) Manuelli and Ricca-Rosellini, *Gazz. chim. ital.*, 29, II. 135 (1899)

water, showed the double melting point which has been reported for **trimethylisomelamine,**[11] namely, **123–124°** and **179°;** yield, 41.3%.

Anal. Calcd. for trimethylisomelamine: N, 50.00. Found: **N, 49.41.** The filtrate from the trimethylisomelamine, on precipitation with ammonium **picrate,** gave **11.8** g. **(40.2%)** of **N,N′-dimethylguanidine picrate,** m. p. 178° after **recrystallization** from water.

Ten grams of *n*-**butyl-nitroguanidine,** 20 g. of *n*-**butylamine,** and **150** cc. of **water** were similarly **refluxed** for twelve hours under pressure and in the presence of carbon dioxide. Two liquid phases remained. The aqueous phase, on precipitation with **ammonium picrate,** yielded **11.05** g. **(42.4%)** of N,N^t-di-n-butylguanidine **picrate,** m. p. 122.5° after recrystallization from benzene. The oily phase, consisting probably of **tri-*n*-butylisomelamine,** could not be made to **crystallize.**

Ten grams of **benzyl-nitroguanidine, 20** g. of benzylamine, and **150** cc. of water were similarly **refluxed** for fifteen hours. The solution on cooling deposited a white solid which, collected, dried and recrystallized from *n*-**butyl** alcohol, yielded 5.95 g. of **tri**benzylisomelamine **(46.3%). Strakosch**[12] previously prepared this substance but did not report the melting point. We find that it melts first at **146–147°,** then solidifies, and finally melts again with decomposition at **157–158°.**

Anal. Calcd. for **tribenzylisomelamine:** N, **21.21.** Found: N, 21.01, 20.92. The dibenzylguanidine in the reaction mixture was **not** determined because of the **difficulty** of separating its **picrate** from the **picrate** of benzylamine.

Action of Concentrated **Sulfuric** Acid on Alkylguanidine Nitrates.—Four grams of **methylguanidine** nitrate was stirred slowly into **5** cc. of concentrated sulfuric acid cooled in a freezing mixture. The resulting thick paste was drowned in **30 cc.** of cracked ice and water, and the material which precipitated, recrystallized once from alcohol, yielded **3.2 g. (91%)** of N-ethyl-N^t-nitroguanidine, m. p. 160–161°, identified by mixed melting point with a known sample, m. p. **160.5–161°.**

Four grams of n-butylguanidine nitrate, by the same procedure, gave **3.1** g. (93%) of **N-*n*-butyl-N′-nitroguanidine,** m. p. 84.5'.

Three grams of **N,N-dimethylguanidine** nitrate, treated similarly with 4 cc. of concentrated sulfuric acid, gave **2.29 g. (87%)** of **N,N-dimethyl-N′-nitroguanidine,** m. p. **194.5°.**

N–n–Heptyl–N–nitroguanidine has not heretofore been described. A sample prepared by the action of 2 cc. of concentrated sulfuric acid on **0.3** g. of **heptylguanidine nitrate** was found to be identical with material prepared from heptylamine and **nitroguanidine,**[2] as follows. Twenty grams of nitroguanidine, **25** g. of n-heptylamine and **100 cc.** of water were heated together in the water-bath at 65–70° for about an hour until all of the nitroguanidine had gone into solution. The reaction mixture was then chilled and saturated with carbon dioxide, and the **heptyl-nitroguanidine** which separated was collected and recrystallized from alcohol to constancy of melting point at 115°, **5** g. (13.5%).

Anal. Calcd. for heptyl-nitroguanidine: N, **27.92.** Found: **N,** 27.86, 27.87.

The **filtrate** from the carbon dioxide treatment was divided into two portions. One portion on precipitation with ammonium **picrate** gave n-heptylguanidine **picrate,** light yellow needles from **20% alcohol,** m. p. **140.5'.** The other, evaporated to dryness and treated with dilute nitric acid, yielded n-heptylguanidine nitrate, stout colorless needles from water, m. p. **86".** The total amount of heptylguanidine obtained from this experiment was **38%.**

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(11) Freund and **Schwartz,** *Ber.*, 99,2498 (1896); **McKee,** *Am.* Chem *J.*, 36,208 (1906).

(12) **Strakosch,** *Ber.*, **5,** 694 (1872).

Nitration of Alkylguanidine Sulfates.—Three grams of methylguanidine sulfate was slowly stirred into 5 cc. of concentrated sulfuric acid chilled in a freezing mixture, 2.50 g. of potassium nitrate was added, the mixture was allowed to stand for five minutes and was drowned in 30 cc. of cracked ice and water. The product, after recrystallization from alcohol, amounted to 2.15 g. (75%) of N-methyl-N′-nitroguanidine.

An experiment with 2.15 g. of n-butylguanidine sulfate, 5 cc. of concentrated sulfuric acid and 1.85 g. of potassium nitrate yielded 1.95 g. (87%) of N-*n*-butyl-N′-nitroguanidine.

One with 3 g. of N,N-dimethylguanidine sulfate, 5 cc. of concentrated sulfuric acid and 2.43 g. of potassium nitrate gave 2.09 g. (75%) of N,N-dimethyl-N′-nitroguanidine.

Five grams of guanidine sulfate, 10 cc. of concentrated sulfuric acid, and 4.80 g. of potassium nitrate gave 4.18 g. (87%) of nitroguanidine.

Attempts to Nitrate N,N′,N″-Trimethylguanidine Nitrate.—Three grams of N,N′,N″-trimethylguanidine nitrate was stirred slowly into a mixture of 4 cc. of concentrated sulfuric acid and 2 cc. of nitric acid (1.42). Eighty-six per cent. of the material was recovered in the form of picrate. Three grams of the nitrate was added to 10 cc. of absolute white nitric acid; after half an hour at room temperature the mixture was drowned—and 78% of the material was recovered. Two grams of the nitrate, evaporated to dryness on the steam-bath with 20 cc. of absolute nitric acid, left a residue of 1.4 g. of the unchanged nitrate.

Action of Phosphoric Acid on Guanidine Nitrate.—Twenty cc. of 85% phosphoric acid was mixed with a 50 cc. volume of phosphorus pentoxide, 5 g. of guanidine nitrate was added, and the mixture was heated to 65° and held there for thirty minutes without signs of decomposition. When the mixture was drowned, there was no precipitate and 97% of the guanidine was recovered in the form of picrate.

Similar mixtures were allowed to stand at room temperature for periods up to thirty hours, and in each case 95% or more of the guanidine was recovered. A mixture which stood for forty-eight hours at room temperature, and was then drowned, yielded 3.5 g. (82%) of nitroguanidine.

Summary

N-Alkyl-N′-nitroguanidines dearrange in aqueous solution to form alkylcyanamides from which N,N′-dialkylguanidines may be produced by combination with primary amines. The tendency of the alkylcyanamides to hydrolyze or to polymerize impairs the usefulness of the synthesis. If the reaction mixtures are acidified with acetic acid to *P*H about 6.13, yields of 40–50% of the dialkylguanidines may be obtained.

The hydrolysis of the N-alkyl-N′-nitroguanidines is really the hydrolysis of their dearrangement products.

Monoalkylguanidines and N,N-dialkylguanidines nitrate on the nonalkylated nitrogen atom. We have not been able to nitrate other alkylguanidines.

The mechanism of the nitration is evidently not loss of water from the nitrate.

The basicity of guanidine and its derivatives is evidently a property of the molecule as a whole and not a property of any particular nitrogen atom.

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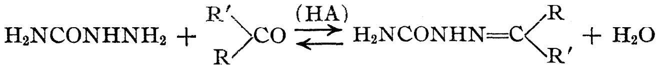
Semicarbazone Formation, and the Incomplete Dissociation of a Salt of the Ammonium Type

BY PAUL D. BARTLETT[1]

Semicarbazone formation is a reaction of a base with a neutral compound, catalyzed by an acid



$$H_2NCONHNH_2 + \begin{matrix}R'\\ \\ R\end{matrix}\!\!>\!CO \overset{(HA)}{\rightleftarrows} H_2NCONHN{=}C\!<\!\!\begin{matrix}R\\ \\ R'\end{matrix} + H_2O$$

The rate of the reaction, in very dilute aqueous solution, is proportional to the concentration[2] of each of these three molecular species. In the absence of unexpected complications, this proportionality should be maintained at least up to a 0.5 M concentration of the catalyst, as in the well-known cases of general acid catalysis.[3]

However, in the case of furfural reacting with semicarbazide under the catalytic influence of acetic acid, the relationship between acid concentration and rate of reaction is a linear one only below 0.05 M acid.[4] Above this value the curve (shown in Fig. 1) flattens off rapidly with increasing acid concentration, until at an acid concentration of 0.42 M the reaction rate constant is only one-fifth of that predicted from the values at the lowest concentrations. These measurements were made in different dilutions of an acetic acid–sodium acetate buffer, the PH and ionic strength being kept constant. · In buffers of the concentration used, the catalytic effect of the hydrogen ion is much less than that of the undissociated acetic acid.

The type of curve which represents this abnormal behavior is just that which would be expected if the salt, semicarbazide acetate, were not completely dissociated in aqueous solution, but existed in an undissociated molecular form in increasing amount with increasing concentration of free acetic acid. If this were the case, the relationship at any PH between the bimolecular velocity constant k and the acid concentration [HA] should be

$$k = k_{\rm h} + \frac{b[{\rm HA}]}{[{\rm HA}] + K_{\rm m}} \qquad (1)$$

$K_{\rm m}$ is the dissociation constant of the salt into molecular acid and molecular base, $k_{\rm h}$ is the reaction rate due to hydrogen ions, and b is the constant upper limit approached by the second term of the equation.

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(1) National Research Fellow.

(2) Conant and Bartlett, THIS JOURNAL, 64, 2881 (1932).

(3) A strictly linear relationship between acid concentration and reaction rate was found by Dawson, Hall, and Key [*J. Chem. Soc.*, 2847 (1928)] for the iodine-acetone reaction catalyzed by acetic acid up beyond 0.5 *M*. Bronsted and Guggenheim [THIS JOURNAL, 49, 2573 (1927)] measured the rate of the mutarotation of glucose with formic acid up to 0.25 M, also without deviations from the linear relationship.

(4) Conant and Bartlett, Ref. 2, p 2890

The constant k_h is a difficult quantity to measure, since this reaction requires buffered solutions in order to yield velocity constants and therefore cannot be run in dilute strong acids. The value of k_h in the present case can be estimated by extrapolation from the first two points on the curve. The value so obtained is 8.8.

In Fig. 1 is shown the curve for Equation (1) when $k_h = 8.8$, $b = 149$ and $k_m = 0.119$. The closeness of fit of this curve supports the hypothesis of incomplete dissociation of the salt.

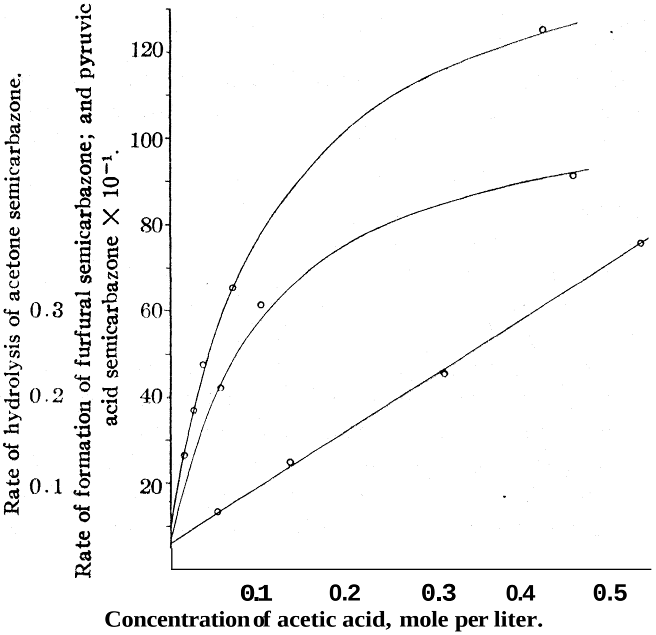

Fig. 1.—Reaction rate as a function of acetic acid concentration at 25°: upper curve, furfural + semicarbazide; middle curve, pyruvic acid + semicarbazide; lower curve, acetone semicarbazone + water.

That this non-linear relationship between reaction rate and catalyst concentration does not occur when semicarbazide is not one of the reactants is shown by the rates of hydrolysis of acetone semicarbazone at different concentrations of an acetate buffer of *P*H 4.60. Here the rate is a linear function of the acid concentration up past 0.5 *M* (Fig. 1), as in the case of other acid-catalyzed reactions.

Equation (1) would fit equally well if the incomplete dissociation in question were that of a *furfural* acetate. However, if such a product existed in mobile equilibrium with its dissociation products, with as small a dissociation constant as 0.12, it could be easily prepared by dissolving furfural in glacial acetic acid. There is no noticeable heat effect on mixing these two liquids; and no product can be recovered from the solution except the furfural and acetic acid themselves.

A further evidence that the equilibrium measured concerns the semicarbazide, and not the aldehyde, is offered by three rate measurements on the formation of pyruvic acid semicarbazone in acetate buffers of different concentrations. Application of Equation (1) yields a value of K_m within 10% of that determined from the runs with furfural. If K_m does not vary with the nature of the carbonyl compound involved in the reaction, then the carbonyl compound does not enter into the measured equilibrium. The similarity of the curves of rate against acid concentration is shown in Fig. 1. The constants for the case of pyruvic acid are $k_h = 64$, $b = 1060$ and $K_m = 0.108$.

Since the successes of the Debye–Hückel theory, salts of the ammonium type have been generally regarded as completely dissociated in aqueous solution, and this is believed to be the first case where the dissociation constant of such a salt has been subject to measurement. This is not a favorable case for conductivity methods because of the high degree of "hydrolysis" of the salt. The positive ion of semicarbazide has $pK_A = 3.66$ at 25° at $\mu = 0.08$.[5] Acetic acid has $pK_A = 4.63$ at the same ionic strength.[6] Very closely, then, in any solution of semicarbazide acetate

$$\frac{[\mathrm{H_2NCONHNH_2}]\,[\mathrm{CH_3COOH}]}{[\mathrm{H_2NCONHNH_3^+}]\,[\mathrm{CH_3COO^-}]} = 10 \qquad (2)$$

Therefore if the molecular dissociation constant

$$K_m = \frac{[\mathrm{H_2NCONHNH_2}]\,[\mathrm{CH_3COOH}]}{[\mathrm{H_2NCONHNH_3OOCCH_3}]} = 0.12$$

then the ionic dissociation constant

$$K_i = \frac{[\mathrm{H_2NCONHNH_3^+}]\,[\mathrm{CH_3COO^-}]}{[\mathrm{H_2NCONHNH_3OOCCH_3}]} = 0.012$$

Since semicarbazide is only very slightly soluble in benzene (0.003 g. in 100 cc.), an attempt was made to measure the dissociation of semicarbazide acetate by distribution of acetic acid between benzene and an aqueous solution of semicarbazide acetate. But it was found that the presence of a small amount of acetic acid renders semicarbazide much more soluble in benzene. A molar solution of acetic acid in benzene will dissolve 0.5 g. of semicarbazide per 100 cc., or 160 times as much as pure benzene will dissolve. This disturbance is sufficiently great to render the distribution method unreliable.

Application to Preparation of Semicarbazones.—The incomplete dissociation of semicarbazide acetate has the consequence that the equilibrium reached in the hydrolysis of a semicarbazone, beside being determined by PH in the manner found by Conant and Bartlett,[2] depends also

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[5] Bartlett, THIS JOURNAL, **54**, 2853 (1932). By an error in the manuscript, the correct values 3 68 at 24° and 3.66 at 25° appear interchanged in this paper.

[6] Cohn, Heyroth and Menkin, *ibid.*, **50**, 696 (1928).

upon the concentration of undissociated acid in acetate, and probably in varying degree also in other buffers. If we neglect the reaction due to hydrogen ion, which is a small fraction of k in strong buffer solutions, we may write the approximate equations

$$k' = c[\mathrm{HA}] \qquad (3)$$

which defines c, the specific catalytic constant of the acid HA in the hydrolysis of the semicarbazone, and

$$k = \frac{b[\mathrm{HA}]}{[\mathrm{HA}] + K_m} \qquad (4)$$

then the equilibrium constant K for the hydrolysis is given approximately by

$$K = \frac{c}{b}(K_m + [\mathrm{HA}]) \qquad (5)$$

Therefore in preparing semicarbazones in the usual manner, from semicarbazide hydrochloride and sodium acetate, the yield is diminished if the acetic acid concentration is allowed to rise much above the value of K_m, or 0.12. When the acid is at this concentration, the rate of formation of the semicarbazone is, by Equation (1), at more than half its maximum value for that buffer, so that any advantage of having more acid present is more than offset by unfavorable effects on the equilibrium.

Theoretical Part

Derivation of Equation (I).—At a constant PH a constant fraction of the semicarbazide present is in the free-base form. Dividing the observed velocity constants by this fraction gives these constants referred to the free-base form. The constants appearing in the tables have been so corrected. We may then, for simplicity, assume that the solution contains only the form $H_2NCONHNH_2$ (represented SH_2) in equilibrium with acetic acid (HA) and the undissociated salt (SH_3A). The dissociation constant of the latter is defined as

$$K_m = [\mathrm{SH_2}]\,[\mathrm{HA}]/[\mathrm{SH_3A}] \text{ whence}$$
$$[\mathrm{SH_3A}] = [\mathrm{SH_2}]\,[\mathrm{HA}]/K_m$$

Assuming that SH_3A is unreactive, the velocity constant due to HA as a catalyst, $(k - k_h)$, will be proportional to the fraction

$$[\mathrm{SH_2}]/([\mathrm{SH_2}] + [\mathrm{SH_3A}])$$

and to [HA]. Since HA in this work is a buffering acid, and its concentration is large compared to that of SH_3A, we may write

$$k - {}_hk - a\,\frac{[\mathrm{SH_2}]\,[\mathrm{HA}]}{[\mathrm{SH_2}] + [\mathrm{SH_3A}]}$$

where a is a proportionality constant. Substituting from above for $[SH_3A]$, we have

$$k - k_h = a\,\frac{[\mathrm{SH_2}]\,[\mathrm{HA}]}{[\mathrm{SH_2}](1 + [\mathrm{HA}]/K_m)} = \frac{aK_m\,[\mathrm{HA}]}{K_m + [\mathrm{HA}]}$$

Defining $b = aK_m$

$$k - k_h = \frac{b[\mathrm{HA}]}{[\mathrm{HA}] + K_m} \quad (1)$$

For the purpose of fitting to data, Equation (1) is thrown into the form

$$b - \frac{k}{[\mathrm{HA}]} K_m = k - k_h$$

and the unknowns b and K_m are determined by the solution of normal equations formed from the several observations.

The Temperature Coefficient.—One of the unusual characteristics of the semicarbazone reaction is its very low temperature coefficient which, in the case of acetone reacting with semicarbazide in a phosphate buffer of PH 7, corresponds to a heat of activation of only 2500 calories. It has seemed plausible to regard this reaction as between one of the molecular species involved and a binary complex in equilibrium with the other two. If this complex were formed with evolution of heat, its greater dissociation at the higher temperatures would work to counteract its increased reaction rate in formation of the final product, thus explaining the low over-all temperature coefficient of the reaction.

One is therefore on the lookout for a complex in equilibrium with any two of the reactants in semicarbazone formation. With the discovery that molecular semicarbazide acetate exists in equilibrium with semicarbazide

TABLE I

RATE OF FORMATION OF FURFURAL SEMICARBAZONE AT 25.00 ± 0.01° AS A FUNCTION OF ACETIC ACID CONCENTRATION (DATA OF CONANT AND BARTLETT)

Fit of the equation $k = 8.8 + \frac{149[\mathrm{HA}]}{[\mathrm{HA}] + 0.119}$

[HA]	(k − 8.8) calcd.	k(calcd.)	k(obs.)	Deviation, %
0.0173	18.9	27.7	26.4	4.9
.0273	27.8	36.6	37.0	1.1
.0395	37.1	45.9	47.4	3.2
.0718	56.0	64.8	65.3	0.8
.424	116.1	124.9	125.4	0.4
			Average	2.1

The observed constants of Conant and Bartlett have been divided by 0.85, to be expressed in terms of pure SH2 rather than a mixture of SH_2 and SH_3^+.

TABLE II

RATE OF FORMATION OF PYRUVIC ACID SEMICARBAZONE AT 25.00 ± 0.01° AS A FUNCTION OF ACETIC ACID CONCENTRATION

Fit of the equation $k = 64 + \frac{1060[\mathrm{HA}]}{[\mathrm{HA}] + 0.108}$

[HA]	(k − 64) calcd.	k (calcd.)	k (obs.)	Deviation, %
0.0585	372	436	420	3.8
.104	520	584	613	4.4
.457	857	921	915	0.6
			Average	2.9

TABLE III

RATE OF FORMATION OF FURFURAL SEMICARBAZONE AT 0.1 ± 0.1° AS A FUNCTION OF ACETIC ACID CONCENTRATION

Fit of the equation $k = 5.5 + \frac{84[HA]}{[HA] + 0.115}$

[HA]	(k − 6.5) calcd.	k (calcd.)	k (obs.)	Deviation, %
0.0259	15.5	21.0	22.1	5.0
.0568	27.8	33.3	31.6	5.4
.100	39.2	44.7	44.2	1.1
.148	47.3	52.8	49.9	5.8
.248	57.5	63.0	65.3	3.5
.405	65.6	71.1	72.6	2.1
			Average	3.8

and acetic acid, the hypothesis that this may be the desired intermediate, however improbable, deserves consideration.

Semicarbazide acetate is ruled out as the kind of intermediate sought, by the fact that K_m, determined from a set of buffer-dilution rate measurements with furfural at 0°, has the same value within the experimental accuracy as at 25°. It will be noticed, however, that on account of the constant ratio between $[HA][SH_2]$ and $[SH_3A]$, Equation (1) would apply equally well if SH_3A were the reactive form and SH_2 and HA were inactive.

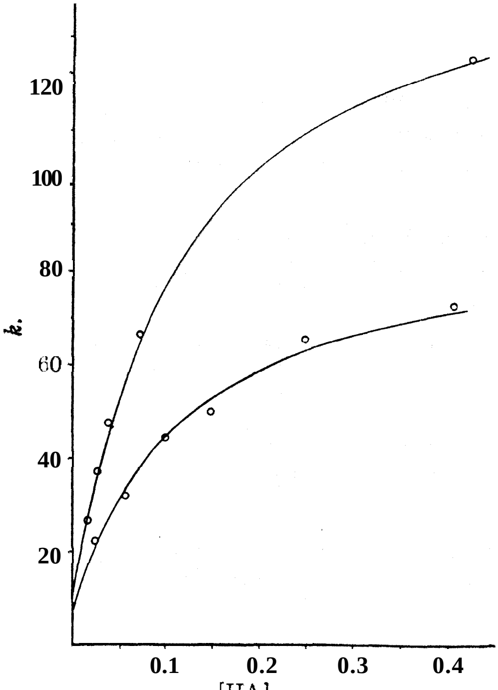

Fig. 2.—Rate of formation of furfural semicarbazone as a function of acetic acid concentration: upper curve, 25°; lower curve, 0°.

In Fig. 2 the curves of catalyst concentration *vs.* rate of reaction in formation of furfural semicarbazone at 25 and at 0° are shown. Extrapolation of the data at 0° yields a k_h of about 14, and direct application of the three-constant equation (1) gives a value of 8.3. It may be that the hydrogen-ion catalyzed reaction has a zero or negative temperature coefficient (Kilpatrick and Kilpatrick[7] have shown that the heat of activation of the mutarotation of glucose varies by as much as 1700 calories with different catalysts). But in

[7] Kilpatrick and Kilpatrick, THIS JOURNAL, 68, 3698 (1931)

this case, in view of the limited accuracy of extrapolation from the data, it seems more legitimate to estimate k_h at 0° by ascribing the same fraction of the catalysis at a given concentration to the hydrogen ion as at 25°. This has been done, and the value $k_h = 5.5$ is used in the calculations. This reaction should prove rewarding to more accurate physico-chemical study.

The constants obtained at 0° are $k_h = 5.5$, $b = 84$ and $K_m = 0.115$. The fit of the equation to the data is shown in Table III.

Question of the Reaction Path.—This reaction brings out clearly a fact inherent in all acid and basic catalysis. Consistent results have been obtained from the first by treating the reaction as if it were between the uncharged, basic form of semicarbazide and the ketone or aldehyde, catalyzed by the uncharged acetic acid. However, in any solution containing both a base B and an acid HA, on account of the equilibria

$$\mathrm{B} + \mathrm{H}^+ \qquad \mathrm{BH}^+ \text{ and}$$
$$\mathrm{A}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{HA}$$

there is, independent of PH, a constant ratio

$$[\mathrm{B}][\mathrm{HA}]/[\mathrm{BH}^+][\mathrm{A}^-]$$

a relationship of which Equation (2) is the expression in the present case. It follows that any formulation of a reaction as an acid catalysis of any base, however weak, can be replaced by a formulation of the same reaction as a basic catalysis of the *conjugate acid* of the substrate. Semicarbazone formation might equally well be described as a reaction of the ion $H_2NCONHNH_3^+$, catalyzed by the acetate ion. None of the kinetic methods at our disposal will distinguish between the possible reaction paths.

If the temperature coefficient of this reaction had first been measured in acid solution, or if the basic catalysis interpretation had been applied, the heat of activation would have had the not unusual value of 14,100 calories, instead of the 3100 calculated from the rates at 0.100 M acid, in Tables I and III. This follows from the change in the relative acidity constants of the semicarbazide ion and acetic acid with the temperature, from which the heat value

$$\mathrm{H_2NCONHNH_2 + CH_3COOH \longrightarrow H_2NCONHNH_3^+ + CH_3COO^-};$$
$$\mathrm{AH} = -11{,}000 \text{ calories}$$

is obtained. Thus, the *pair of ions* $H_2NCONHNH_3^+$ and CH_3COO^- fulfil the thermodynamic criterion for an "intermediate" in the reaction, but this fact does not advance our knowledge of the mechanism.

Experimental Part

The velocity measurements on the hydrolysis of acetone semicarbazone and the formation of furfural and pyruvic acid semicarbazones were carried out in the manner previously described. Three acetate buffer solutions were used,[2] in varying dilutions.

Use	[HA]	[NaA]	PH
Pyruvic acid runs	0.475	0.302	4.39
Furfural runs	.515	.515	4.59
Acetone semicarbazone runs	.467	.467	4.60

The ionic strength in these runs was not held constant, since the salt effect in the reaction is slight. However, this necessitates corrections in the more dilute solutions for the fact that the pK_A for semicarbazide ion changes with ionic strength in the opposite direction to the pK_A of acetic acid. pK_A for semicarbazide ion was taken as 4.40 above $\mu = \mathbf{0.08}$ at 0°, and was assumed below $\mu = \mathbf{0.08}$ to be equal to $\mathbf{4.26} + {}^1/_2\sqrt{\mu}$.

For the runs at 25°, a thermostat regulated within 0.01° was used, and for the runs at 0°, an ice-bath.

The concentration of semicarbazide was determined by titration at PH 7 with **0.02** N iodine. Five titrations were made during the course of a velocity run. The mean deviation of the constants in any one run was from **0.6** to **3.8%.** The condensation velocity constants were corrected by dividing each by the fraction of the semicarbazide in the free-base form at the PH of the reaction.

TABLE IV

DATA TO ILLUSTRATE DETERMINATION OF VELOCITY CONSTANTS FURFURAL 4 SEMICARBAZIDE AT 0.1 ± 0.1°

49.8 cc. buffer, 100 cc. water, 4.96 cc. each of 0.1604 M furfural and 0.0919 M semicarbazide **hydrochloride.** $y_0 = $ **0.00499 (furfural);** $x_0 = $ **0.00285** ($[SH_2] + [SH_3^+]$); **[HA] + 0.148; PH** = **4.59**

$$kt = 1005 \log_{10} \frac{x + 0.002238}{x - 0.000055} + C$$

Minutes	Sample, cc.	Iodine, cc.	x	Fraction	Log	k	Dev.	%
1.15	10	4.57	0.00228	2.026	0.3066			
5.71	10	2.66	.1326	2.804	.4478	31.1	0.7	
10.72	10	1.65	.823	3.985	.6004	30.7	.3	
15.28	10	1.17	.583	5.345	.7279	29.8	.6	
20.12	10	.81	.405	7.55	.8779	30.1	.3	
210+	20	0.27 .18 .23 .20			Average	30.4	.5	1.6

whence equilibrium $K = 0.00004$

The solubility of semicarbazide in benzene, with and without acetic acid, was determined by extracting aliquot portions of the saturated benzene solution with **0.1** N hydrochloric acid, and titrating the extract, after bringing to PH 7 with **0.02** N iodine: **2** cc. of saturated semicarbazide in benzene required **0.22** cc. of iodine; **2** cc. of saturated semicarbazide in 1 N benzene–acetic acid took **29.0** cc. of iodine solution, at 25°.

The data for hydrolysis rate of acetone semicarbazone as a function of catalyst concentration are given in Table V.

TARLE V

KATE OF HYDROLYSIS OF ACETONE SEMICARBAZONE AT 25°, AS A FUNCTION OF ACETIC ACID CONCENTRATION, PH 4.60

[HA]	*k*	No. of detns.	Mean deviation, %
0.0550	u.0672	5	1.6
.1375	.124	3	3.2
.311	.226	5	3.1
.535	.379	2	0.8

The author is appreciative of the helpful interest shown in this work by Drs. D. A. MacInnes, Theodore Shedlovsky, and A. S. Brown, and by Professor V. K. La Mer; and is especially indebted to Professor J. M. Nelson for the hospitality of his laboratory, where this work was carried out.

Summary

1. Evidence is found that sernicarbazide acetate, a salt of the ammonium type, is incompletely dissociated in aqueous solution, from the dependence of the rate of semicarbazone formation on acetic acid concentration.

2. The dissociation constant of this salt into molecules has the approximate value 0.12, both at 25 and at 0°.

3. Consequences of this new equilibrium effect, for semicarbazone preparation and for the mechanism of the reaction are discussed.

NEW YORK, N. Y.

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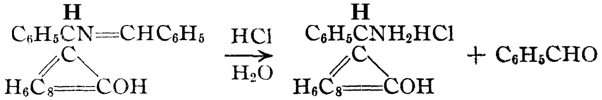
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OP THE UNIVERSITY OF CINCINNATI]

The Betti Condensation. Effect of Substituents on the Stability and Optical Rotation of the Resulting Amines

BY FRANCIS EARL RAY AND WILLIAM A. MOOMAW

In 1900 Mario Betti first reported the condensation of benzaldehyde, ammonia and β-naphthol to give a Schiff base, I. On hydrolysis with hydrochloric acid phenyl-β-naphtholaminomethane hydrochloride and benzaldehyde resulted,' II.



I II

The reaction was extended by the use of primary amines instead of ammonia, and quite recently Littman and Brode[2] have further extended the application to secondary amines.

Betti[3] in a study of optical rotation has condensed his amine with sub-

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(1) Betti, *Gazz chim. ital*, 80, II, 310 (1900); 31, I, 386 (1901)

(2) Littman and Brode, THIS JOURNAL, 52, 1655 (1930).

(3) Betti, *Gazz chim ital*, 36, TI, 392 (1906); 37, I, 63 (1907): 46, I, 200 (1916); 50, II, 276 (1920)

stituted aldehydes and measured the rotation of the resulting Schiff base, but, in so far as we have been able to find, no one has investigated the use of substituted benzaldehydes in the original condensation with ammonia and β-naphthol.

This investigation was undertaken to test the general applicability of Betti's condensation. In the present paper the condensation of ortho-, meta- and para-chlorobenzaldehydes with ammonia and 8-naphthol is discussed together with a preliminary report on the use of nitrobenzaldehydes.

Betti's amine is readily decomposed, especially in alkaline solution, to give benzaldehyde and 8-naphthol. The benzaldehyde thus liberated combines with a molecule of the amine to form the original Schiff base. It was hoped that by the use of substituted benzaldehydes more stable amines would result. Just the opposite has, however, proved to be the case.

The reaction of the three monochlorobenzaldehydes followed closely that of benzaldehyde but the resulting amines were less stable than the amine from the unsubstituted aldehyde. The order of stability was: H > *m*-Cl > o-CI > *p*-Cl.

The chloro substituted amines were also much more difficult to separate into their optical antipodes. Tartaric acid, which effects a satisfactory resolution of the unsubstituted amine, gives with the chloro compounds an insoluble racemic salt. The ortho and meta compounds were finally resolved with the aid of 1-malic acid but the para resisted all efforts at resolution. The order of optical activity was: *o*-Cl > *m*-Cl > H > *p*-Cl(?).

The *p*-chloro compound could not be resolved. There are two probable explanations: the most usual of which is that the right conditions were not obtained; the other, which we favor, is that the instability of this amine precluded its resolution. While satisfactory resolution of the dextro form of the ortho and meta chloro compounds was possible, it was extremely difficult to obtain the more soluble levo antipodes in a state of purity. Even evaporation of an ether solution at room temperature caused some decomposition and racemization of the amines.

When the nitrobenzaldehydes were mixed with β-naphthol and alcoholic ammonia they reacted to the extent of 90% or more with the ammonia to give the nitrohydrobenzamide. In the case of the m-nitrobenzaldehyde in addition to the hydrobenzamide a small amount of a compound melting at 198° was recovered. This is now under investigation and will be the subject of a subsequent paper.

Evidently as the substituents increase in negativity there is less tendency for the 8-naphthol to take part in the reaction.

Experimental Part

***m*-Chlorophenyl-β-naphtholaminomethane.**—Eleven grams (1 mol equiv) of P-naphthol was dissolved in 25 cc. of 95% alcohol to which 20 g. (2 mol equiv.) of *m*-

chlorobenzaldehyde was added. The flask was cooled and saturated with ammonia gas. After standing for twenty-four hours the contents had changed to an almost solid viscous substance which, when treated with a few drops of ether and stirred, changed to fine yellowish crystals. The crystals were washed six times with small portions of alcohol which left 23 g. (82%) of pure white crystals melting at 109°.

Anal. Calcd. for $C_{24}H_{17}Cl_2ON$: C, 70.94; H, 4.19; Cl, 17.47; N, 3.45. Found. C, 70.53; H, 4.25; Cl, 17.30; N, 3.34.

The amine hydrochloride was prepared by steam distilling 15 g. of the condensation product suspended in 20 cc. of 6 *N* hydrochloric acid; 11.5 g. (96%) of the m-chlorophenyl-6-naphtholaminomethane hydrochloride was obtained from the acid solution; decomposition temperature, 220 to 230°.

Anal. Calcd. for $C_{17}H_{15}ONCl_2$: Cl, 22.17. Found: Cl, 22.40.

To prepare the free racemic amine 10 g. of the amine hydrochloride was treated in an ice mixture with a 25% solution of potassium hydroxide. From 3 to 5 cc. of ether was added and stirred until the amine formed a flocculent precipitate which was immediately filtered and washed free from alkali with water; yield 7 g. (77%) of m-chloro-β-naphtholaminomethane melting at 124–125°.

Anal. Calcd. for $C_{17}H_{14}ONCl$: C, 71.94; H, 4.94; Cl, 12.51; N, 4.94. Pound: C, 72.12; H, 4.85; Cl, 12.68; N, 5.23.

o-Chlorophenyl-β-naphtholaminomethane.—The condensation product was prepared as described for the meta compound; m. p. 165–167°. After recrystallizing the material once from chloroform and once from benzene it melted rather sharply at 173° (uncorr.).

Anal. Calcd. for $C_{24}H_{17}Cl_2ON$: C, 70.94; H, 4.19; Cl, 17.47. Found: C, 70.87; H, 4.42; Cl, 17.69.

o-Chlorophenyl-6-naphtholaminomethane hydrochloride was prepared by steam distilling 30 g. of the original condensation product with hydrochloric acid as described for the m-chloro derivative; 21 g. (88%) of the amine hydrochloride was obtained; decomp. temp. 185 to 190°. Analysis was made from a sample recrystallized twice from hydrochloric acid solution.

Anal. Calcd. for $C_{17}H_{15}ONCl_2$: C, 63.77; H, 4.69; Cl, 22.17. Found: C, 63.93; H, 4.79; Cl, 21.79.

The free amine was prepared as described for the meta derivative. Five and five-tenths g. (62%) of a cream colored amine was obtained, m. p. 129–130°. After recrystallization twice from ether and once from acetone it was almost pure white and melted at 133–134".

Anal. Calcd. for $C_{17}H_{14}ONCl$: C, 71.97; H, 4.94; Cl, 12.51. Found: C, 72.24; H, 5.22; Cl, 12.76.

***p*-Chlorophenyl-β-naphtholaminomethane.**—The condensation product was prepared as described for the meta compound; m. p. 150".

Anal. Calcd. for $C_{24}H_{17}Cl_2ON$: C, 70.94; H. 4.19; Cl, 17.47. Found: C, 71.64; H, 4.27; Cl, 17.33.

Six grams of the condensation product was subjected to steam distillation in a suspension of hydrochloric acid; 4.3 g. (91%) of the whitish flaky amine hydrochloride was obtained; decomp. temp. 190 to 195°.

Anal. Calcd. for $C_{17}H_{15}Cl_2ON$: Cl, 22.17. Found: Cl, 22.40.

The free *p*-chloro amine was prepared from the hydrochloride as previously described. The ether extract yielded 2.5 g. (80%) of the white crystalline amine, m. p. 120".

Anal. Calcd. for $C_{17}H_{14}ClON$: Cl, 12.51. Found: Cl, 12.94.

Resolution of the Racemic **Amines**

The *m*-chlorophenyl-β-naphtholaminomethane was resolved into its optically active antipodes by treating 5.3 g. (1 mol) of the amine in 130 cc. 95% alcohol with 2.5 g. (1 mol) of *l*-malic acid; 2.7 g. of the salt was obtained. The liquid was further evaporated by an air current and agitated until crystals began to separate which yielded 2.8 g. of the more soluble salt. The salt obtained in the first fraction was hydrolyzed and about 2 g. of the d-amine was filtered and washed free of alkali with distilled water; m. p. not sharp at 126'.

In a 1-dm. tube 0.0667 g. of the dry amine in 10 cc. of ethyl ether gave α_D +0.53°, α^{25}_D +79.5°.

The *l*-amine was obtained by hydrolyzing the second fraction to yield 2.1 g. of the *l*-amine; m. p. 122°. This material gave a rotation of —0.37' with 0.0667 g. of the amine dissolved in 10 cc. of ether at room temperature, using a 1-dm. tube, $[\alpha]^{25}_D$ —55.5'.

The last crystalline salt fraction from the above yielded the l-amine on hydrolysis with the same specific rotation as that obtained from the salt of the second fraction. An attempt was made to increase the specific rotation of the l-amine above —55.5°, first by recrystallizing the salt before hydrolysis, and finally by use of Ingersoll's method,' but a more complete resolution was never effected.

Resolution of the o-chlorophenyl-8-naphtholaminomethane was carried out as described for the meta compound. Hydrolysis of the salt obtained in the first fraction was accomplished as described above. The optical rotation of the ether solution taken in a 1-dm. tube was +0.65°, and 10 cc. of the solution contained 0.0722 g. of the amine, α^{25}_D +89.8'.

Hydrolysis and extraction of the 0.67 g. of salt from the second fraction was accomplished as described previously: 0.1207 g. in 10 cc. of ether in a 1-dm. tube gave α_D —1.01°, $[\alpha]^{25}_D$ —83.7°.

Attempts to recrystallize the *l*-acid-*l*-base only resulted in a less active amine.

Summary

1. The Betti condensation of aromatic aldehydes, ammonia and β-naphthol has been applied to the mono-chlorobenzaldehydes.
2. Of the three resulting amines the ortho and meta compounds have been resolved into their active forms.
3. The nitrobenzaldehydes gave chiefly the corresponding hydrobenzamides.
4. Due to the instability of the chlorophenyl-β-naphtholamines and the difficulty encountered in their resolution, these bases are less useful as resolving agents than the unsubstituted amine.

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(4) Ingersoll, THIS JOURNAL, 47, 1168 (1925)

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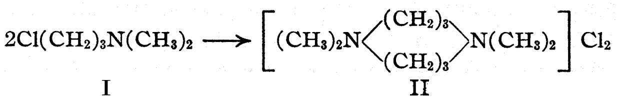
Quaternary Ammonium Salts from Halogenated Alkyl Dimethylamines. II. The Polymerization of Gamma-Nalogenopropyldimethylamines

BY C. F. GIBBS, E. R. LITTMANN AND C. S. MARVEL

Amines of the type $Br(CH_2)_nN(CH_3)_2$ have been found to react intramolecularly to produce cyclic quaternary ammonium salts in those cases where n has the value 4, 5 and 6.[1] Previously, Knoor and Roth[2] had studied the product formed when γ-chloropropyldimethylamine (I) was allowed to polymerize in aqueous solution and had assigned an eight-membered ring structure (II) to the quaternary ammonium salt thus obtained.

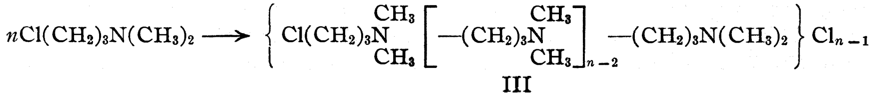


I II

In support of this structure they showed that alkaline decomposition of the quaternary ammonium salt gave allyldimethylamine, tetramethyltrimethylenediamine and an oxygen containing compound believed to be isoallyl ether $(CH_2{=}C(CH_3))_2O$ formed by the hydration of allene $CH_2{=}C{=}CH_2$ which was expected as a primary decomposition product in the reaction.

It was also reported in the earlier work that when the chloro amine reacts with itself in water solution, the alkalinity of the solution diminishes but never completely disappears. It has now been found that the product resulting from this polymerization reaction is definitely basic and, moreover, contains some chlorine that is not ionic. These two facts cannot be explained by the cyclic formula (II) suggested by Knoor and Roth.

An alternative formula (111), which in view of the recent work of Carothers[3] on other bifunctional reactions seems to be more logical than the cyclic structure, does satisfactorily account for these reactions of the quaternary ammonium salt as well as for the alkaline decomposition products obtained by Knoor and Roth.



$$n\mathrm{Cl(CH_2)_3N(CH_3)_2} \longrightarrow \left\{ \mathrm{Cl(CH_2)_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}} \left[-\mathrm{(CH_2)_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}} \right]_{n-2} -\mathrm{(CH_2)_3N(CH_3)_2} \right\} \mathrm{Cl}_{n-1}$$

III

A long chain molecule of the type indicated in formula III would still contain one chlorine atom which was of the alkyl halide type and one tertiary amine group which would make the molecule basic. From the ratio of the non-ionic chlorine to ionic chlorine in the product it has been

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[1] Littmann and Marvel, THIS JOURNAL, 52,287 (1930).

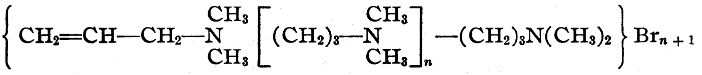
[2] Knoor and Roth, Ber., 39,1425 (1906).

[3] See Carothers [Chem. Rev., 8,353 (1931)] for a review of this field.

possible to estimate a mean molecular weight for the polymer. The mean value for n in the above formula falls between 12 and 13 and the approximate molecular weight is 1500. An attempt to check this value by titration of the amine group gave a value of about 4000 for the molecular weight.

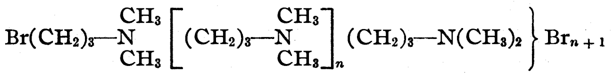
Some experiments on the polymerization of γ-bromopropyldimethylamine have given further evidence that linear polymerization is a characteristic reaction of the halogenopropyldimethylamines. A sample of the bromo amine of the correct bromine content gave a polymeric salt with less bromine in the molecule than was present in the amine. The product was always slightly basic and contained some non-ionic bromine. The low total bromine content suggested that during polymerization a side reaction was taking place which involved the loss of hydrogen bromide and the formation of an olefinic linkage. This surmise was corroborated by the fact that an aqueous solution of the polymer decolorized bromine water and potassium permanganate solution. A sample of the polymer was treated with silver nitrate in water solution and the resulting nitrate still contained a small amount of bromine. When this nitrate was treated with bromine evidence for the addition of bromine to the molecule was obtained.

The properties of this polymeric product are best explained by assuming it to be a mixture of the two types of compounds shown in formulas IV and V. Since the product obtained is a mixture no molecular weight could be calculated from the analytical data.



$$\left\{CH_2{=}CH{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{N}}\left[(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}}\right]_n{-}(CH_2)_3N(CH_3)_2\right\}Br_{n+1}$$

IV



$$\left\{Br(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}}\left[(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}}\right]_n(CH_2)_3{-}N(CH_3)_2\right\}Br_{n+1}$$

V

Experimental

γ-Phenoxypropyldimethylamine.—This amine was prepared by the general procedure of Knoor and Roth.[2] To a solution of 63 g. of dimethylamine in absolute alcohol was added 75 g. of phenoxypropyl bromide. The mixture was allowed to stand overnight, and then warmed on the steam-bath under a reflux condenser for about a half hour. The excess dimethylamine and the alcohol were distilled from a steam-bath, the residue in the flask was treated with an excess of 25% aqueous sodium hydroxide solution and the amine was collected in ether. On distillation 51 g. (81.5% of the theoretical amount) of a product boiling at 130–132° (20 mm.) was obtained.

The chloroplatinate was prepared by dissolving a sample of the amine in dilute hydrochloric acid and adding a slight excess of chloroplatinic acid. The derivative was crystallized from dilute alcohol and then melted at 147°.

Anal. Subs., 0.1693: Pt, 0.0430. Calcd. for $(C_{11}H_{17}ON)_2\cdot H_2PtCl_6$: Pt, 25.42. Found: Pt, 25.40.

When a large excess of dimethylamine was not used, a considerable amount of a product which seemed to be diphenoxypropyldimethylammonium bromide was formed.

γ-Chloropropyldimethylamine.—The method of Knoor and Roth[2] was used for this preparation. The yield was 4.5 g. of chloro amine from 12.5 g. of the phenoxy compound. The product boiled at 124–126". A picrate melting at 105° was prepared. The melting point reported before was 110°.[2]

γ-Bromopropyldimethylamine.—A solution of 20 g. of γ-phenoxypropyldimethylamine in 140 cc. of concentrated hydrobromic acid was distilled in an all-glass apparatus until the temperature of the vapors reached 123–125°. A second portion of about 100 cc. of hydrobromic acid was added and the distillation repeated. If necessary a third and even a fourth portion of hydrobromic acid was used and distillation was continued until no more phenol distilled with the water, thus showing that the cleavage of the ether was complete. The residue in the flask was evaporated to dryness under reduced pressure and the bromo amine hydrobromide was dissolved in about 30 cc. of water. This solution was cooled and treated with an excess of cold 28% aqueous sodium hydroxide solution. The bromo amine was collected in ether and separated. The ether was removed by evaporation under reduced pressure and the bromo amine was then distilled as rapidly as possible. It boiled at 51° (15 mm.); 34–35' (6 mm.) Some polymerization occurred during distillation but the yield of distilled amine was 14 g. (75% of the theoretical amount); d_4^{20} 1.2312; n_D^{20} 1.4602.

Anal. Subs., 0.3496: 20.51 cc. of 0 1028 *N* $AgNO_3$. Calcd. for $C_5H_{12}NBr$: Br, 48.18. Found: Br, 48.20.

A sample of the hydrobromide was purified from absolute alcohol and analyzed.

Anal. Subs., 0.4925: 38.47 cc. of 0.1028 N $AgNO_3$. Calcd. for $C_5H_{13}NBr_2$: Br, 64.72. Found: Br, 64.32.

The chloroplatinate of the arnine decomposed slowly at 125–130°.

Anal. Subs., 0.0557: Pt, 0.0144. Calcd. for $[C_5H_{12}NBr]_2 \cdot H_2PtCl_6$: Pt, 26.13. Found: Pt, 25.85

Polymer of **γ-Chloropropyldimethylamine.**—Knoor and Roth[2] prepared the quaternary ammonium salt by allowing an aqueous solution of the chloro amine to stand for some time. The same compound was obtained by heating the liquid amine on the steam cone for about thirty-six hours. The solid which formed was washed with ether to remove a little unchanged amine and then purified by dissolving in anhydrous methyl alcohol and precipitating with ethyl acetate. The yield of quaternary ammonium salt from 1.5 g. of amine was 0.7 g. This compound melted with decomposition at 242–243°. The chloroaurate melted at 247–250° (Maquenne block) and the chloroplatinate at 275–280° (Maquenne block). The salts melted much lower if slowly heated in an oil-bath. Knoor and Roth have reported these salts as melting at 247–248° and 275–276°, respectively. The quaternary ammonium salt was amorphous. Its aqueous solution was alkaline toward methyl orange.

Anal. (Parr bomb) Subs., 0.1732: 78.19 cc. of 0.01826 *N* $AgNO_3$. Calcd. for $(C_5H_{12}NCl)_x$: Cl, 29.22. Found: Cl, 29.23. (Volhard) Subs., 0.1930: 81.72 cc. of 0.01826 N $AgNO_3$. Found: ionic Cl, 26.89.

From the ratio of non-ionic chlorine to total chlorine 2.39/26.89 it can be seen that the molecular weight of the polymer must he twelve to thirteen times the molecular weight of the simple substance or approximately 1500. Titration with standard acid gave a higher value.

Titration. Subs., 0.3321: 4.4 cc. of 0.0175 *N* HCl. Molecular weight: 4309.

Polymerization of **γ-Bromopropyldimethylamine.**—The bromo amine was polymerized by heating the pure liquid at steam-bath temperatures; by allowing the liquid to stand at room temperature; by allowing the solution in ethyl alcohol to stand at room temperature and at 0 to −10°; and by allowing the solution in anhydrous ether to stand at room temperature. The polymeric material which was formed under these various conditions did not vary greatly in physical properties. It was a white, non-crystalline, very hygroscopic solid which melted at temperatures varying from 225 to 240° with some decomposition. The water solution was distinctly basic to methyl orange but titration with standard acid gave unsatisfactory results. Samples were purified for analysis by dissolving the crude material in 90% methyl alcohol and precipitating the polymer with ethyl acetate. Very little product was lost. The samples were dried over phosphorus pentoxide in an Abderhalden dryer under reduced pressure at 76°. The properties of typical polymers are listed in Table I.

TABLE I

PROPERTIES OF TYPICAL POLYMERIC QUATERNARY AMMONIUM SALTS FROM γ-BROMOPROPYLDIMETHYLAMINE

Amine, g.	Conditions of reaction	Yield of polymer, g.	M. p., °C.	Br calcd. for $(C_5H_{12}NBr)_x$	Total Br found, %	Ionic Br found, %
10	Liquid on steam-bath	9	225–240	48.18	45.71	45.11
10	Liquid on steam-bath	9	225–240	48.18	47.17	46.40
10	Liquid on steam-bath	9	225–240	48.18	46.34	44.44
10	Liquid at room temp. (approx. 25°)	9.5	225–240	48.18	46.84	46.07
5	Soln. in 95% alcohol at 32°	3	235–245	48.18	47.37	46.60
10	Soln. in 95% alc. at −10 to 0°	6	230–245	48.18	48.00	46.80
10	Soln. in dry ether at room temp. (approx. 25°)	6	225–240	48.18	46.68	44.00

A I-g. sample of the polymer was heated with an aqueous solution of trimethylamine at 100° in a sealed tube to see if the non-ionic bromine could be converted to ionic bromine. No significant change in ionic bromine could be detected.

A solution of the polymer in water decolorized potassium permanganate solution and also bromine water.

A solution of 2.64 g. of polymer (total Br, 47.37%; ionic Br, 46.6%) in water was made barely acid with nitric acid. A slight excess of aqueous silver nitrate was added and the silver bromide was filtered from the solution. The filtrate was treated with hydrogen sulfide and the silver sulfide was filtered. The filtrate was evaporated to dryness in a desiccator and dried in vacuum over phosphorus pentoxide. The nitrate thus obtained weighed 0.6 g. It was a resinous solid which decomposed at about 125° It contained bromine as indicated by the following analysis.

Anal. Subs., 0.1687, 0.2422: 0 69, 1.75 cc. of 0.0213 N $AgNO_3$ Found: Rr, 0 77, 1.05.

A solution of 7.88 g. of the polymer (total Br, 46.65; ionic Br, 45.85) was treated with silver nitrate and the nitrate obtained as described above. The nitrate in water solution was treated with bromine water until a slight excess of bromine remained in solution. This solution was evaporated to dryness and the residue analyzed.

Anal. Subs., 0.2595: 0.91 cc. of 0.1028 *N* $AgNO_3$. Found: Br, 2.95.

This increase of bromine in the nitrate polymer after treatment with bromine water indicates that some bromine had added to an olefinic linkage in the polymer

Summary

1. γ-Chloropropyldimethylamine has been found to react intermolecularly to give a quaternary ammonium salt which contains non-ionic chlorine and which is slightly basic. These facts are not in harmony with

the cyclic structure previously assigned to the quaternary ammonium salt but are satisfactorily explained on the basis of an open chain polymeric structure.

2. γ-Bromopropyldimethylamine has been found to give a similar polymer but a side reaction involving loss of hydrogen bromide occurs along with the simple polymerization reaction.

URBANA, ILLINOIS RECEIVED AUGUST 4, 1932
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Carbon Suboxide

BY CHARLES D. HURD AND FORREST D. PILGRIM

The most satisfactory method for the synthesis of carbon suboxide is the pyrolysis of diacetyltartaric anhydride, details for which have been given by Ott and Schmidt.[1] Yields of 41% (32 g. of the suboxide from an original 250 g.) were obtained when the vapors of the anhydride were distilled at 11 mm. over a hot platinum filament. The specially designed apparatus, which calls for difficult glass blowing, is, however, objectionable. In the present work it was found that even better yields could be realized with simple apparatus and at ordinary pressure.

Carbon suboxide was found to react readily with hydroxylamine, giving malonhydroxamic acid: $O=C=C=C=O + 2NH_2OH \longrightarrow CH_2(CONHOH)_2$. This is analogous to the synthesis of acethydroxamic acid from ketene[2] and hydroxylamine. In a similar way, β-phenylhydroxylamine reacted with carbon suboxide to produce N,N′-diphenylmalonhydroxamic acid, $CH_2(CON(C_6H_5)OH)_2$. No products were isolated wherein carbon suboxide and the hydroxylamine added to each other except in the ratio of 1:2.

Experimental Part

A Pyrex combustion tube (1 cm. inside diam.) was constricted at one end and sealed to the side arm of a 50-cc. Pyrex distilling flask[3] which carried a dropping funnel in the stopper. Previously the tip of the funnel had been drawn out to a capillary. The tube was then placed within an electric furnace (36 cm. long, but longer furnaces have also been employed satisfactorily). The tube was closed with a one-holed stopper into which fitted a bent tube leading downward into a flask. A two-holed stopper closed this flask. A vertical, water-cooled condenser was fitted into the other hole. From the top of the condenser, the gases were delivered into a receiver which was cooled to −78° by solid carbon dioxide and acetone. Any gases which were still uncondensed were passed through an aniline trap. The exhaust gases, which contained much carbon monoxide, were conducted into a hood or outdoors.

Fifty grams of diacetyltartaric anhydride, which was readily made by the method of

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[1] Ott and Schmidt, *Ber*., 55, 2126 (1922); Ott, *ibid.*, 47, 2391 (1914).

[2] Hurd and Cochran, THIS JOURNAL, 45, 515 (1923).

[3] A larger flask could, of course, be used if desired.

Wohl and Oesterlin,[4] was placed in the distilling flask, melting the crystals within the flask whenever necessary. The empty reaction tube was then heated to a temperature of 625–650° and a salt-bath (or oil-bath) at 150° was placed around the distilling flask. Mercury was put in the dropping funnel and dropped at a constant rate into the molten anhydride. In this manner the latter was forced through the hot tube at a constant rate during two and a half hours. This gave a contact time in the hot zone of about fourteen seconds.

The liquid which was condensed by the water condenser weighed 33 g. By distillation these fractions were obtained: to 115°, 3.0 g.; 118–125° (acetic acid), 18.2 g.; 125–130°, 6.4 g.; residue, 5.4 g. No diacetyltartaric anhydride was recoverable from the residue.

The carbon suboxide[5] which was condensed in the −78° trap weighed 5.5–7.0 g. Another 0.8 g. was indicated since 2.5 g. of malonanilide was obtained from the aniline trap. This yield of 6.3–7.8 g. represents a yield of 35–49%. On redistillation shortly after its preparation, most of the product came over at 6–7°. A trace of hydroquinone, added to this distillate, was effective in retarding polymerization.

It was found advisable to remove the carbon deposit in the combustion tube fairly often, although not necessarily after each 50-g. run.

Carbon Suboxide and Hydroxylamine.[6]—One and a half cubic centimeters of liquid carbon suboxide was added dropwise to 1.8 g. of hydroxylamine,[7] the tube for which was kept in a bath at −15°. Each drop of the ketene caused a vigorous reaction. The product formed had the appearance of a yellow wax. With ferric chloride solution it gave an intense purple coloration, typical of hydroxamic acids. The solid was left in a vacuum desiccator over sulfuric acid for two days to remove the excess of hydroxylamine, after which it crystallized readily from hot water; m. p. 154–155° with decomposition. This is known[8] to be the melting point of malonhydroxamic acid, $CH_2(CONHOH)_2$. The yield was 1–1.5 g.

About 0.05 g. of the hydroxamic acid was dissolved in water and 2–3 drops of ammonium hydroxide added. After a short time, a copious precipitate of the characteristic acid ammonium salt separated. It melted with decomposition at 140°.

Carbon Suboxide and β-Phenylhydroxylamine

First.—A cold solution (0°) of 1.07 g. (0.01 mole) of β-phenylhydroxylamine in 5 cc. of ethyl acetate was added slowly to a cold solution of 0.7 cc. of carbon suboxide (0.01 mole) in 5 cc. of ethyl acetate. Crystals separated in about five minutes but the solution was left for an hour before filtering. The yield was about 1.2 g.; m. p. 128°.

Second.—This was like the first except that 2.14 g. (0.02 mole) of β-phenylhydroxylamine was taken with the 0.7 cc. of carbon suboxide. Crystals formed as before. Melting point, mixed melting point and analytical data showed that the products formed in the two cases were identical, namely, N,N′-diphenylmalonhydroxamic acid, $CH_2(CON(C_6H_5)OH)_2$.

Anal. Subs. 0.1997 (from first), 0.1939 (from second); CO_2, 0.4580, 0.4449; H_2O, 0.0820, 0.0803. Calcd. for $C_{15}H_{14}O_4N_2$: C, 63.0; H, 4.9. Found: C, 62.7, 62.6; H, 4.6, 4.6.

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[4] Wohl and Oesterlin, *Ber.*, 34, 1144 (1901).

[5] This preparation has been confirmed several times in this Laboratory by Dr. R. K. Summerbell and Mr. G. W. Klingaman.

[6] Some preliminary work on this problem was performed by Mr. Fred W. Sackett in 1922.

[7] Prepared by the method of Hurd and Brownstein, THIS JOURNAL, 47, 67 (1926).

[8] Hantzsch, Schatzmann and Urbahn, Ber., 27, 799, 803 (1894).

Summary

A simplified method is described for the synthesis of carbon suboxide from diacetyltartaric anhydride. Carbon suboxide reacts with hydroxylamine and with β-phenylhydroxylamine giving, respectively, malonhydroxamic acid and N,N'-diphenylmalonhydroxamic acid.

EVANSTON, ILLINOIS RECEIVED AUGUST 5, 1932
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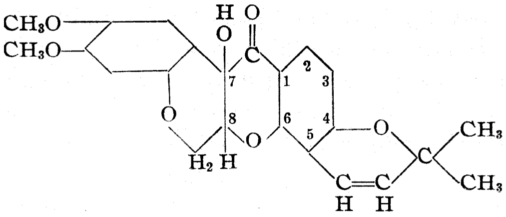
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Tephrosin. III. Some Acidic Derivatives of Tephrosin

BY E. P. CLARK

Evidence has been presented[1] to show that tephrosin may be represented by formula I or the isomeric form in which the hydroxyl group is on carbon atom 8.



I. Tephrosin, $C_{23}H_{22}O_7$

An isomeric form of tephrosin has also been described,[2] and facts have been recorded indicating that the difference between the isomers must be sought in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8.

In this connection a hitherto unrecorded observation, which if anything confuses rather than clarifies the problem, should be presented.

In the first paper of this series,[3] tephrosindicarboxylic acid, m. p. 220°, was described. It was prepared by permanganate oxidation of tephrosin and was separated from the manganese dioxide as the potassium salt with the aid of boiling absolute alcohol. When the manganese dioxide remaining after the treatment with alcohol was again extracted with hot water, an isomeric tephrosindicarboxylic acid was obtained as the potassium salt. The free acid was obtained crystalline by acidifying the solution with a mineral acid.

When freshly crystallized and air dried the new acid melted at 127–128° and contained three mols of water of crystallization. Upon exposure to air for some time the melting point usually became 140–142°, but when it

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(1) Clark, THIS JOURNAL, **54**, 3000 (1932).

(2) Clark and Claborn, *ibid.*, 54, 4454 (1932)

(3) Clark, *ibid.*, **53**, 729 (1931).

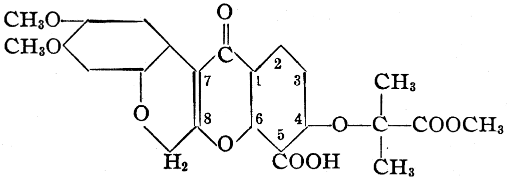
was dried in a vacuum or in an oven at 90° the acid became anhydrous and melted at 175–177°.

The new acid was thus shown to be distinctly different from the first tephrosindicarboxylic acid whose melting point was 220° and which crystallized anhydrous. The reactions of the new substance, however, were the same as those of the tephrosindicarboxylic acid previously described. For example, boiling a diphenyl ether solution of either acid for a short time gave the same tephrosinmonocarboxylic acid, the formula of which was suggested in a previous communication.' Also esterification of either acid gave the same half ester of an anhydro derivative of tephrosindicarboxylic acid. These observations indicate that whenever the hydrogen and hydroxyl groups on carbon atoms 7 and 8 are removed as water with the coincident formation of a dehydro derivative, the products are identical.

Isotephrosin also yields a dicarboxylic arid Isomeric with the two acids from tephrosin, and all evidence concerning the three materials indicates that the structural difference between them exists in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8.

Because experimental data are lacking and the possibility of securing information relative to the configurations under discussion is small, it seems unjustifiable to do more than to record the facts as presented.

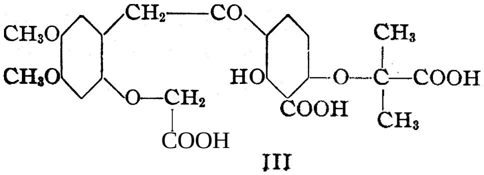
Reference should be made, however, to some derivatives of the materials here considered. It was stated before that both tephrosindicarboxylic acids yield the same half ester of an anhydro derivative of tephrosindicarboxylic acid. This ester, which from analogy should be called a half ester of dehydrodeguelindicarboxylicacid, is undoubtedly represented by II.



II

The fact that only one carboxyl group is esterified is in harmony with the structure presented, as the carboxyl group on carbon atom 5 is diortho substituted and is therefore resistant to esterification.

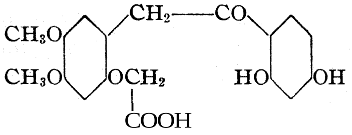
Alkaline alcoholic hydrolysis caused the typical splitting of the molecule at the double bond as well as the removal of the ester group and yielded a tricarboxylic acid which from analogy may be represented by III.



III

This acid melted at 178–179° and gave a brownish-red color reaction with ferric chloride.

In the last communication upon deguelin[1] reference was made to tephrosic acid. At that time there was not sufficient material to complete the study of the compound. This, however, has since been done, and it has been found that tephrosinmonocarboxylic acid readily undergoes alkaline alcoholic hydrolysis yielding tephrosic acid, but in the process the carboxyl group on carbon atom 5 is removed so that tephrosic acid is undoubtedly represented by IV.



IV. Tephrosic acid, $C_{18}H_{18}O_8$

Experimental

Tephrosindicarboxylic Acid (m. p. 127–12S°).—Tephrosin (5 g.) was oxidized with potassium permanganate as outlined in the first communication of this series.[1] After the manganese dioxide was thoroughly extracted with boiling absolute alcohol, it was digested with about 500 cc. of boiling water. The manganese dioxide was removed by filtration, and the filtrate was concentrated under reduced pressure to approximately 100 cc. The liquid was then heated to boiling, acidified with sulfuric acid and allowed to crystallize. One and seven-tenths grams of crude acid was usually obtained. This material was always somewhat contaminated with a dark tarry substance. It was found, however, that this could be readily removed by dissolving the crude acid in a slight excess of alkali and boiling the solution with a small quantity of hydrogen peroxide until the color of the solution cleared. The hot liquid (approximately 100 cc.) was then acidified to Congo red with dilute sulfuric acid and allowed to crystallize. The acid separated as cauliflower-like groups of colorless crystals which melted at 127–128°. When these crystals were exposed to the air for some days the melting point was usually found to be 140–142°. Upon drying the acid in a vacuum or in an oven at 90° the material became anhydrous and at the same time acquired a light green color. It then melted with decomposition at 175–177". It was optically inactive.

Anal. Calcd. for $C_{23}H_{22}O_{11}.3H_2O$: mol. wt., 528.3; C, 52.26; H, 5.34; OCH_3 (2), 11.75. Found: mol. wt. (titration), 529; C, 52.15; H, 5.45; OCH_3, 11.7. For the anhydrous material. Calcd.: OCH_3, 13.1. Found: OCH_3, 13.0.

Tephrosinmonocarboxylic Acid from Tephrosindicarboxylic Acid (m. p. 127–128°).—This material was obtained from the 127–128° melting acid in exactly the same manner as previously recorded for the acid which melts at 220°.[1] The yields were essentially the same, and the preparation was shown by melting point, mixed melting point, and the ferric chloride test to be tephrosinmonocarboxylic acid.

Esterification of the Tephrosindicarboxylic Acid (m. p. 127–12S°).—One gram of the dicarboxylic acid was refluxed for one hour with 25 cc. of a 5% absolute methyl alcoholic solution of hydrochloric acid. Almost at the beginning of the reaction the solution acquired a yellow color (dehydro formation), and after a short time a considerable quantity of yellow crystals separated. At the end of the time specified the liquid was cooled, and the crystalline material was removed by filtration. It was then recrystallized from hot 75% methyl alcohol. Thus obtained it consisted of thin yellow needles, which, as they were heated, became intensely yellow at approximately 150° and then melted at 220–221°.

Anal. Calcd. for $C_{24}H_{22}O_{10}$: mol. wt., 470.3; C, 61.26; H, 4.72; OCH_3 (3), 19.8. Found: mol. wt. (titration), 499; C, 61.20; H, 4.93; OCH_3, 19.7.

The same product, identified by melting point and mixed melting point, was obtained by applying the above-described procedure to tephrosindicarboxylic acid (m. p. 220°).

Hydrolysis of the Compound Described Above.—Two hundred and thirty mg. of the half ester described above was boiled for thirty minutes with 5 cc. of 10% alcoholic potassium hydroxide solution. The liquid was then diluted with water and acidified with sulfuric acid. The tricarboxylic acid (formula III) separated as long colorless rods. The yield was 195 mg. The melting point of the air-dried substance was 90–95°. However, the material contained solvent of crystallization and gradually effloresced. The thoroughly dried compound melted at 178–179°. It gave a brownish-red color reaction with ferric chloride.

Anal. Calcd. for $C_{23}H_{24}O_{12}$: C, 55 96; H, 4.91; OCH_3 (2), 12.5. Found: C, 55.77; H, 5.31; OCH_3, 12.5.

Tephrosic Acid.—Tephrosic acid was prepared according to the directions previously recorded. Nine-tenths gram of tephrosinmonocarboxylic acid yielded 0.66 g of crude tephrosic acid. It was recrystallized by acidifying a boiling, slightly alkaline solution of the potassium salt with dilute sulfuric acid. Its melting point was 196–197°.

Anal. Calcd. for $C_{18}H_{18}O_8$: mol. wt.. 362.2; C, 59.66; H, 5.01; OCH_3 (2), 17.1. Found: mol. wt. (titration), 353; C, 59.36; H, 5.23; OCH_3, 17.0.

Summary

Permanganate oxidation of tephrosin yields two isomeric dicarboxylic acids whose structural differences consist in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8 (formula I in the text).

Several other acidic derivatives of tephrosin are described, and their relation to the structure of tephrosin is discussed.

WASHINGTON, D. C

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Phototropic and Thermotropic Anils from 5-Bromosalicylaldehyde

BY C. M. BREWSTER AND L. H. MILLAM

This article is a record of further investigation of anils with a view to increasing the number of compounds exhibiting phototropy and thermotropy. While over three hundred anils have been examined and the majority found to be thermotropic, only twenty-two are reported to be phototropic.[1] The condensation products of aldehydes and primary amines called anils have the general formula R—CH=N—R′. Fifteen of the anils previously reported to be phototropic are derivatives of salicylaldehyde. We have found three new phototropic anils, one a derivative of salicylaldehyde and two of 5-bromosalicylaldehyde. The introduction of the negative bromine atom in salicylaldehyde inhibited to some extent the tendency toward forming phototropic anils, and when two bromine atoms were introduced the resulting anils no longer exhibited phototropy.

In the following table, the plus sign indicates that the anil is phototropic; it is followed by reference number to the literature. The zero indicates that the anil has been examined but is not phototropic. Where a reference number appears at the head of a column only, this applies to the other compounds in the column.

It is apparent that anils of aldehydes having the hydroxyl group para to the aldehyde group may be phototropic, as well as those with the hydroxyl group in the ortho position, and we are studying further examples in this series. The anils from *p*-bromoaniline show phototropy, whether the hydroxyl group is ortho or para to the aldehyde group. Replacement of the ortho hydroxyl group by an ortho nitro group inhibits the phototropy. If the para bromine atom of the amine is replaced by chlorine, the resulting anil is not phototropic.

There is a great variation in the time required for the reversible change due to light or dark. With 5-bromosalicylidene-α-naphthylamine there is a discernible darkening on exposure to sunlight for as short an interval as five minutes, and this fades to the original pale yellow color after the compound is kept in the dark for an hour. However, salicylidene-β-naphthylamine requires an hour's exposure to sunlight to change from yellow to red, and the compound does not change back to the yellow color unless kept in the dark for some weeks. Prolonged exposure to actinic light, however, induces permanent polymorphic change in some of the anils. No indication of phosphorescence or triboluminescence was observed.

Of the twenty-eight new anils which we have prepared, twenty-two were

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(1) Excellent summaries of the work on phototropy may be found in articles by Stobbe. *Chem Z.*, 44, 340 (1920); and by Chalkley, *Chem. Rev.*, 6, 207 (1929).

TABLE I

PHOTOTROPIC ANILS

Amines	Aldehydes Salicylidene-	o-Nitrobenzylidene-	4-Hydroxybenzylidene-	2-Hydroxy-3-methoxybenzylidene-	3,5-Dibromosalicylidene-	5-Bromosalicylidene-
Aniline	+[a]	0[c]	0[f]	0[d]	0[h]	0[i]
o-Bromoaniline	+[d]	0	*0*	0		*0*
m-Bromoaniline	+[d]	0	0	0		
p-Bromoaniline	+[d]	0	+	*0*	0	+
o-Chloroaniline	+[b]	+	0	0		0
m-Chloroaniline	0[b]	+	0	0		0
p-Chloroaniline	0	0	0	0		0
m-Toluidine	+[a]	*0*	0	*0*		0
o-Anisidine	+[d]	0	+	**0**		0
p-Anisidine	+[d]	0	0	0		0
1,3,4-Xylidine	+[b]	0	0	*0*		
1,2,4-Xylidine	0''	+	+	0		0
1,2,5-Xylidine	0[a]	0	0	+		0
α-Naphthylamine	0[a]	0	0		*0*	+
β-Naphthylamine	+[b]	0	0	*0*	0	0
m-Aminobenzoic acid	+[e]	*0*	0			
p-Aminobenzoic acid	+[b]	0	0			0
m-Phenylenediarnine	+[d]	0			0	
p-Aminoethylbenzoate						
o-Aminocinnamic acid	+[g]					
p-Toluidine	+[i]	0	0	0	*0*	*0*

[a] Senier and Gallagher, J. Chem. *Soc.*, 113, 28 (1918). [b] Senier and Shepheard, ibid., 95,441 (1909). [c] Senier and Clarke, *ibid.*, 105,1917 (1914). [d] Senier, Shepheard and Clarke, *ibid.*, 101, 1950 (1912). [e] Stobbe, Ber. *Verhandl.* sachs. Akad. *Wiss. Leipzig,* 74, 161 (1922). [f] Senier and Forster, J. Chem. *Soc.*, 105,2462 (1914). [g] Gallagher, Bull. *soc. chim.*, [4] 29, 683 (1921). [h] **Brewster,** THIS JOURNAL, 46, 2463 (1924) [i] See experimental part of this article.

found to be thermotropic, changing to a deeper color when heated to a temperature near the melting point. On cooling, the lighter color is restored, though this change usually takes place more slowly than that produced by heat. The restoration of the lighter color may also be brought about in some instances by recrystallization, or by dissolving in dilute alkali and reprecipitating with acids.

Experimental Part

5-Bromosalicylaldehyde.—This compound has been prepared by direct action of bromine on salicylaldehyde,[2] and also by brornination in glacial acetic acid.[3] We found that by mixing solutions of bromine and of salicylaldehyde in carbon tetrachloride. and keeping the mixture at the temperature of the steam-bath for an hour, a purer product was obtained. The solution was diluted with three volumes of ligroin, and on cooling beautiful silky crystals separated. After recrystallization from the same solvents, the product melted at 105° corr.

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(2) Piria, *Ann.*, **30,** 171 (1839).

(3) Auwers and Burger. *Ber.*, 37, 3934 (1904).

TABLE II

Name of compound: R = 5-Bromosalicylidene-	Formula	Color and form	Solvent for crvst.	P	Th	M. p. corr., °C.	Analyses, % Calcd.	Analyses, % Found
R-*o*-toluidine[a]	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Yellow needles	Alcohol	0		86.5	Br, 27 55	Br, 27.56
R-*m*-toluidine[b]	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Golden plates	Alcohol	0		103	Br, 27.55	Br, 27.36
R-*p*-toluidine	$HOC_6H_3BrCH{=}NC_6H_4CH_3$	Yellow plates	Alcohol	0	+	163.5	Br, 27.55	Br, 27.76
R-α-naphthylamine	$HOC_6H_3BrCH{=}NC_{10}H_7$	Pale yellow needles	Alcohol	+	+	109.5	Br, 24.51	Br, 24.88
R-β-naphthylamine[c]	$HOC_6H_3BrCH{=}NC_{10}H_7$	Yellow needles	Bz. + ligroin	0	+	157	Br, 24.61	Br. 24.77
R-*p*-phenetidine	$HOC_6H_3BrCH{=}NC_6H_4OC_2H_5$	Yellow-green needles	Alcohol	0	+	156	Br, 25.00	Br, 24.82
R-*o*-anisidine	$HOC_6H_3BrCH{=}NC_6H_4OCH_3$	Orange needles	Alcohol	0	+	110	Br, 31.25	Br, 31.08
R-*p*-anisidine	$HOC_6H_3BrCH{=}NC_6H_4OCH_3$	Yellow plates	Alcohol	0	+	156	Br, 31.25	Br. 31.32
R-*p*-aminoazobenzene	$HOC_6H_3BrCH{=}NC_6H_4N{=}NC_6H_5$	Yellow-brown scales	Alc., red. from nitrobz.	0	0	212	Br, 21.05	Br, 20.82
R-2-aminoazo-5-toluene	$HOC_6H_3BrCH{=}N(2)CH_3(1)C_6H_3{-}N(5)N(2)C_6H_4CH_3(1)$	Orange-red needles	Nitrobz. + alc.	0	+	212	Br, 19.58	Br, 19.27
R-o-aminophenol	$HOC_6H_3BrCH{=}NC_6H_4OH$	Golden-brown scales	Alcohol	0	+	192.5	Br, 27.36	Br, 27.39
R-p-aminophenol	$HOC_6H_3BrCH{=}NC_6H_4OH$	Orange plates	Alcohol	0	+	239	Br, 27.36	Br. 27.58
R-amino-2 5-xylene	$HOC_6H_3BrCH{=}NC_6H_3(CH_3)_2$	Yellow plates	Alcohol	0	+	67	Br, 26.25	Br, 26.04
R-amino-2'4-dimethylbenzene	$HOC_6H_3BrCH{=}NC_6H_3(CH_3)_2$	Light orange needles	Alcohol	0	+	131.5	Br, 26.25	Br, 26.21
R-*p*-aminobenzoic acid	$HOC_6H_3BrCH{=}NC_6H_4COOH$	Brilliant orange needles	Alcohol	0	+	282	Br, 25.00	Br, 25.27
R-m-nitraniline	$HOC_6H_3BrCH{=}NC_6H_4NO_2$	Orange-red rosets	Bz. + ligroin	0	0	169		Br, 24.70
R-*p*-nitraniline	$HOC_6H_3BrCH{=}NC_6H_4NO_2$	Light orange needles	Bz. + ligroin	0	+	205	Br, 24.91	Br, 25.05
R-aniline[d]	$HOC_6H_3BrCH{=}NC_6H_5$	Orange plates	Alcohol	0	+	122.5		
R-o-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Light orange needles	Alcohol	0	+	88	Br, 25.76 Cl, 11.41	X, 36.96
R-*m*-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Glistening yellow scales	Alcohol	0	+	127.5	Br, 25.76 Cl, 11.41	Br, 25.51 Cl, 11.52
R-*p*-chloroaniline	$HOC_6H_3BrCH{=}NC_6H_4Cl$	Yellow needles	Alcohol	0	+	158	Br, 25.76 Cl, 11.41	Br, 25.18 Cl, 11.51
R-*o*-bromoaniline	$HOC_6H_3BrCH{=}NC_6H_4Br$	Dark orange needles	Alcohol	0	0	78	Br, 45.04	Br, 44.85
R-*p*-bromoaniline	$HOC_6H_3BrCH{=}NC_6H_4Br$	Lustrous yellow leaflets	Bz. + ligroin	+	+	178	Br, 45.04	Br, 44.92
R-2,4-dichloroaniline	$HOC_6H_3BrCH{=}NC_6H_3Cl_2$	Orange needles	Bz. + ligroin	0	+	148	Br, 23.19 Cl, 20.58	X, 43.51
R-2,5-dichloroaniline	$HOC_6H_3BrCH{=}NC_6H_3Cl_2$	Pale yellow needles	Alcohol	0	+	139	Br, 23.19 Cl, 20.58	X, 43.47
Bis-R-*p* phenylenediamine	$(HOC_6H_3BrCH{=})_2N_2C_6H_4$	Lustrous yellow plates	Nitrobz. + alc.	0	+	277	Br, 33.75	Br, 33.58
Bis-R-*m*-toluylenediamine	$(HOC_6H_3BrCH{=})_2N_2C_6H_3CH_3$	Pale cream plates	Nitrobz. + alc.	0	+	186	Br, 32.75	Br, 32.92
Bis-R-dianisidine	$(HOC_6H_3BrCH{=})_2(NC_6H_3OCH_3)_2$	Brick-red needles	Nitrobenzene	0	0	279	Br, 25 96	Br, 25.78
Bis-R-*o*-tolidine	$(HOC_6H_3BrCH{=})_2(NCH_3C_6H_3)_2$	Orange needles	Nitrobenzene	0	+	242	Br, 27.68	Br, 27.80
Bis-R-benzidine	$(HOC_6H_3BrCH{=}(NC_6H_4)_2$	Yellow scales	Nitrobenzene	0	+	345	Br, 29.08	Br, 28 93
R-phenylhydrazone[e]	$HOC_6H_3BrCH{=}NNHC_6H_5$	Pearly scales	Alcohol	+	+	151		
Salicylidene-*p*-toluidine .	$HOC_6H_4CH{=}NC_6H_4CH_3$	Yellow needles	Alcohol	+	+	95	N, 6 63	N, 6 43
Salicylidene-*p*-bromoaniline[f]	$HOC_6H_4CH{=}NC_6H_4Br$	Light yellow needles	Alcohol	+	+	110	Br, 28.95	Br, 29.06

[a] A second form, glistening yellow plates, melting at 165°, was obtained when the materials were melted directly without a solvent. [b] A. Senier and P. Gallagher, J. *Chem. Soc.*, **113**, 28 (1918). [c] A. Senier and F. G. Shepheard, J. *Chem. Soc.*, 95,1945 (1909). [d] Haarmann, *Ber.*, 6,339 (1873). [e] Auwers and Biirger, *ibid.*, 37,3934 (1902). [f] Senier, Shepheard and Clarke, J. *Chem. Soc.*, 101, 1950 (1912)

Anal. Calcd. for $C_7H_5O_2Br$: Br, 39.77. Found: Br, 39.93.

The anils studied in this investigation are described in Table 11. Of these, twenty-eight compounds have been prepared for the first time, as far as we have been able to ascertain. Most of the compounds are readily formed by heating alcoholic solutions of the aldehyde and base; others require prolonged heating in the solvent. A few were formed only on direct heating, without a solvent. The phototropic and thermotropic properties of each compound are indicated in the table.

The anils formed from *m*-nitraniline, *p*-nitraniline, *p*-bromoaniline, 2,4-dichloroaniline, and *p*-phenylenediamine with 5-bromosalicylaldehyde were obtained only on direct fusion without a solvent. The *p*-aminoazobenzene derivative of 5-bromosalicylaldehyde, first obtained from alcohol in the yellow-brown form, on recrystallization from nitrobenzene changes to the red modification. When the red modification is dissolved in acetone and precipitated by addition of alcohol, the yellow-brown modification is again obtained.

Summary

1. A series of twenty-eight new anils, derivatives of 5-bromosalicylaldehyde, has been prepared.

2. Three new instances of phototropy are reported.

3. Twenty-two of the anils are thermotropic.

4. A number of the compounds appear to exist in two forms.

PULLMAN, WASHINGTON

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Asymmetric Syntheses. II. The Action of Optically Active Nitrates on Cyclic Ketones

BY R. L. SHRINER AND E. A. PARKER

The condensation of 4-methylcyclohexanone with d- or *l*-2-octyl nitrite in the presence of sodium ethylate gave an optically active sodium salt of the oxime.[1] This reaction constituted a new type of asymmetric synthesis since the optically active octyl group was split off during a reaction which created an asymmetric carbon atom in the molecule. A second example of this type of asymmetric synthesis has been found in the condensation of 4-methylcyclohexanone and optically active alkyl nitrates.

Previous investigators have shown that alkyl nitrates in the presence of potassium ethylate readily condense with fluorene,[2] phenylacetic ester,[3] α-tetralone[4] and cyclohexanone.[5] In each case the product was the potassium salt of a nitro compound. In the present investigation the potassium salt of a nitro compound was likewise produced in accordance with the reaction

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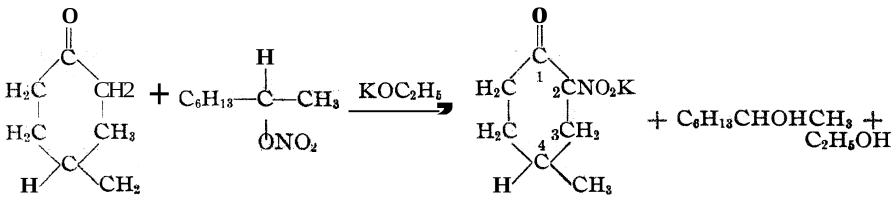
(1) Pezold and Shriner, THIS JOURNAL, 64, 4707 (1932).

(2) Wislicenus and Waldmüller, Ber., 41, 3336 (1908).

(3) Wislicenus and Grützner, *ibid.*, 42, 1930 (1909).

(4) Straus and Ekhard, Ann., 444, 164 (1925).

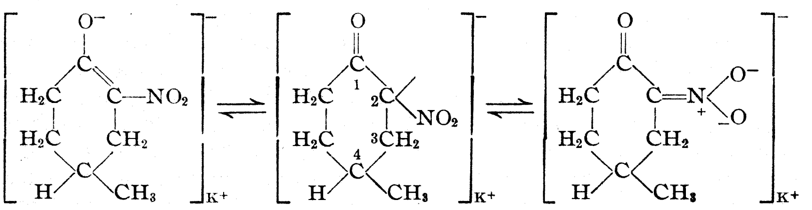
(5) Wieland, Garbsch and Chavan, *ibid.*, 461, 295 (1928).



I II III IV

When an alcohol–ether solution of d-2-octyl nitrate and 4-methylcyclohexanone was treated with potassium ethylate, the dextro potassium salt of ti-nitro-4-methylcyclohexanone (111) precipitated. Similarly the I-2-octyl nitrate yielded the levo potassium salt. That the activity was due to these salts (III) was shown in the first place by the fact that the solid active salts could be isolated and analyzed. Second, it was shown by a control experiment that octanol-2 and potassium-2-octylate (the only other possible optically active products) remained in solution under the experimental conditions used.

This asymmetric synthesis raises a question concerning the location of the optically active center of the molecule (III). The actual cause of the optical activity of these salts may be the fact that carbon atom 4 (Formula III) carrying the methyl group is now asymmetric, in which case this reaction of 4-methylcyclohexanone with active nitrates would be strictly analogous to the previously described reaction with active nitrites.' Or, these compounds may constitute a third example of optically active salts of secondary nitro compounds similar to the salts of d- and 1-2-nitrobutane[6] and d- and I-2-nitro-octane.? The chief evidence in support of this last explanation is the fact that both the *d* and I salts racemized completely in about one hour. It is difficult to explain this rapid racemization if the activity were due to carbon atom 4. If, however, the active salt possesses the structure V, a tautomeric shift to either form VI or VII would readily lead to racemization. This tautomeric shift should not destroy the optical activity if it is due to carbon atom 4, but should destroy any activity due to carbon atom 2.



VI V VII

By carrying out the same reaction on cyclohexanone and an active nitrate it would be possible to decide definitely between the two possibilities.

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(6) Kuhn and Albrecht, Ber.. 60, 1297 (1927).

(7) Shriner and Young, THIS JOURNAL, 52, 3332 (1930)

This condensation **was** carried out but the product was very difficult to isolate. It was produced in poor yields, proved to be very hygroscopic and correct analyses for nitrogen or potassium could not be obtained. **It** was, however, optically active and racemized in about one hour. **A** further study of its preparation and isolation in the pure state is being made.

Experimental

4-Methylcyclohexanone.—This compound was prepared by the oxidation of 4-methylcyclohexanol according to the method previously described,' b. p. 168–170°.

d- **and *l*-Octanol-2.**—Octanol-2 was resolved by fractional crystallization of the **brucine** salts of the acid phthalic ester according to the procedure in "Organic Syntheses."[8] The d-octanol-2 had a rotation of $[\alpha]^{25}_{D}$ +10.15 and the *l*-octanol-2 a rotation of $[\alpha]^{25}_{D}$ −10.30.

***d*-2-Octyl** Nitrate.—A modification of the method of Chapman and Smith[9] was developed for the preparation of this ester in order to avoid the production of octanone-2 noted by Bouveault and Wahl.[10] **A** mixture of 19.5 cc. of concentrated nitric acid, 58.5 cc. of concentrated sulfuric acid and 2 g. of urea was placed in a 400-cc. beaker and cooled to 0° with mechanical stirring. Seventeen and one-half grams of d-octanol-2 ([or]$^{25}_{D}$ +10.15) was added from a separatory funnel through a fine capillary tube reaching to the bottom of the beaker. The temperature was maintained at 0 to 10° with vigorous stirring in an ice–salt bath. The addition of the alcohol took thirty minutes and the mixture was stirred for fifteen minutes longer. The reaction mixture was poured on cracked ice and the colorless oil was separated immediately and washed three times with ice water. The product was dried over anhydrous magnesium sulfate and vacuum distilled at 95–97' at 20 mm. The yield of 15.3 g. was 64.9% of the theoretical. Its rotation was $[\alpha]^{25}_{D}$ +14.59; n^{20}_{D} 1.4301; d^{20}_{20} 0.954; M_D (calcd.), 47.69; M_D (found), 47.39.

Anal. Calcd. for $C_8H_{17}NO_3$: N, 8.00. Found: N, 7.97.

Preparation of 1-2-Octyl Nitrate.—This isomer was obtained by the same procedure as above. Thirty cubic centimeters of concentrated nitric acid, 90 cc. of concentrated sulfuric acid, 3 *g.* of urea and 27 g. of *l*-2-octanol (α_D −10.30°) gave 24.2 g. of ***l*-2-octyl** nitrate which was 66.5% of the theoretical; b. p. 93–94" at 17 mm.; n^{20}_{D} 1.4302; d^{20}_{20} 0.956; M_D (calcd.), 47.69; M_D (found), 47.30; α^{25}_{D} −14.64.

Anal. Calcd. for $C_8H_{17}NO_3$: N. 8.00. Found: N, 8.11.

Preparation of dl-2-Octyl Nitrate.—The racemic 2-octyl nitrate was obtained in the same manner from dl-octanol-2; b. p. 92.5–94.5° at 18 mm.; n^{20}_{D} 1.4299; d^{20}_{20} 0.951; M_D (calcd.), 47.69; M_D (found), 47.51. *Saponification* equivalent. Calcd. for $C_8H_{17}NO_3$, 175. Found: 175.5.

Reaction between **4-Methylcyclohexanone** and dl-2-Octyl Nitrate.—One gram of potassium was dissolved in 8 cc. of absolute ethyl alcohol, 25 cc. of absolute ether was added and the solution placed in a three-necked 200-cc. flask fitted with a mercury-sealed stirrer, condenser, dropping funnel and a thermometer. The apparatus was placed in a water-bath at 40°. A mixture of 4.5 g. of 2-octyl nitrate and 6 g. of 4-methylcyclohexanone dissolved in 70 cc. of absolute ether was added slowly through the dropping funnel with the mixture refluxing. After the ether solution of the ketone and nitrate was added 50 cc. more of absolute ether was added. The mixture was stirred for two more hours, making three hours in all. The yellow precipitate was then filtered.

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(8) "Organic Syntheses," J Wiley and Sons, New York, 1926. Vol. VII, p 68.

(9) Chapman and Smith. J. *Chcm. Soc.*, 20, 581 (1867).

(10) Bouveault and Wahl, *Compt.* rend., 186, 1663 (1903).

washed with absolute ether and dried over phosphorus pentoxide in a vacuum. The yield of 1.5 g. was 29.9% of the theoretical. The crude product contained nitrogen and 24% potassium. Two grams of the crude salt was dissolved in 150 cc. of 95% alcohol, filtered and 300 cc. of absolute ether added. The immediate precipitate was filtered and found to be orange to red in color. A fine yellow precipitate which formed overnight on standing in the ice box was filtered, dried and recrystallized in the same manner.

Anal. Calcd. for $C_8H_{10}NO_3K$: K, 20.03; N, 7.17. Found: K, 21.34; N, 7.05.

Reaction between 4-Methylcyclohexanone and d-2-Octyl Nitrate.—One gram of potassium was dissolved in 7 cc. of absolute alcohol, 25 cc. of absolute ether was added and the solution placed in a 200-cc. three-necked flask fitted with a condenser, mechanical stirrer, dropping funnel and a thermometer. The apparatus was placed in a water-bath at 40°. **A** mixture of 4.5 g. of d-2-octyl nitrate and 6 g. of 4-methylcyclohexanone dissolved in 40 cc. of ether was added slowly through the dropping funnel while the mixture was refluxing. After the ether solution had been added, 50 cc. more of absolute ether was added and the warm mixture stirred for one hour more, making one and a half hours from the beginning. The yellow precipitate was filtered, washed with dry ether and dried over phosphorus pentoxide in a vacuum. The yield of 1.7 g. was 33.9% of the theoretical. For purification one gram of the crude potassium salt was dissolved in 10 cc. of 95% alcohol. The solution was filtered and the salt precipitated by the addition of 300 cc, of dry ether. The immediate precipitate which came down was filtered and the solution allowed to stand in the ice box. After several hours a fine crystalline precipitate separated which was filtered and dried *in vacuo* over phosphorus pentoxide. The salt was a yellow solid which was very hygroscopic. It gave an immediate rotation of $[\alpha]^{25}_{D}$ +9.02° which dropped to zero in 1.1 hours.

Anal. Calcd. for $C_8H_{10}NO_3K$: K, 20.03; N, 7.17. Found: K, 20.95; N, 7.15.

Reaction between 4-Methylcyclohexanone and *l*-2-Octyl Nitrate.—This condensation was carried out in exactly the same manner as the preceding one. The product had a lower rotation of $[\alpha]^{25}_{D}$ −4.00°.

Anal. Calcd. for $C_8H_{10}NO_3K$: K, 20.03; N, 7.17. Found: K, 21.22; N, 7.34.

Reaction between dl-2-Octyl Nitrate and Potassium Ethylate.—The same procedure was used as above except that 4-methylcyclohexanone was omitted. At the end of two hours no precipitate had separated. After standing for two days a slight precipitate separated which was examined and found to be potassium nitrate This experiment shows that potassium 2-octylate was soluble in the concentration of alcohol and ether used as the reaction solvent and hence could not contaminate the salts of the nitro compounds.

Reaction between *l*-2-Octyl Nitrate and Cyclohexanone.—This condensation was carried out by exactly the same procedure as for 4-methylcyclohexanone. After the reaction was complete the orange-brown precipitate was filtered but as soon as the ether was gone the precipitate turned to an oil. Some of the solid left in the flask was suspended in *dry* ether and placed in a vacuum desiccator and the ether evaporated. The solid was dried over phosphorus pentoxide in a vacuum. The material was extremely hygroscopic and turned to an oil in a few minutes if exposed to the air. A sample was weighed out and gave $[\alpha]^{25}_{D}$ −6.72° and the rotation decreased until at the end of one hour it was zero. All attempts to purify the compound and obtain analyses on it have failed up to the present time.

Summary

The reaction between 4-methylcyclohexanone and d- and *l*-2-octyl nitrate in the presence of potassium ethylate produced the d- and l-potassium salts of 2-nitro-4-methylcyclohexanone.

The optical activity of these salts appears to be due to the asymmetry of the carbon atom carrying the nitro group.

URBANA, ILLINOIS RECEIVED AUGUST 8, 1932
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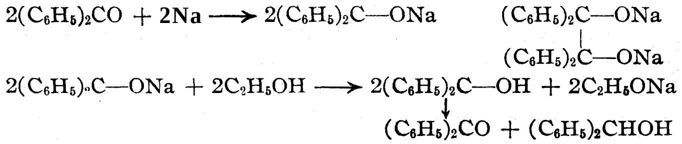
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Mechanism of Reduction by Sodium Amalgam and Alcohol. I. The Reduction of Aromatic Ketones to Hydrols

BY W. E. BACHMANN

During the reduction of benzophenone by 2% sodium amalgam and absolute alcohol two striking phenomena were observed. In the first place, the sodium amalgam is almost without action on the alcohol; when, however, benzophenone is added and the mixture is shaken, a vigorous reaction takes place with evolution of heat and in a few minutes all of the ketone is reduced to hydrol. Secondly, during the reduction the solution becomes blue, indicating the formation of the sodium ketyl $(C_6H_5)_2CONa$; the blue color rapidly disappears if shaking is discontinued. When all of the ketone has been reduced the blue color no longer reappears. When these facts are considered in conjunction with the fact that benzophenone reacts rapidly with sodium amalgam in absence of alcohol and gives the ketyl as the initial product, there can be no doubt that the reduction of the ketone is not effected by the hydrogen liberated by the action of the sodium amalgam on the alcohol; instead, the reduction occurs in virtue of the reactions



$$2(C_6H_5)_2CO + 2Na \longrightarrow 2(C_6H_5)_2C{-}ONa \qquad \begin{array}{c}(C_6H_5)_2C{-}ONa\\ |\\ (C_6H_5)_2C{-}ONa\end{array} \qquad (1)$$

$$2(C_6H_5)_2C{-}ONa + 2C_2H_5OH \longrightarrow \begin{array}{c}2(C_6H_5)_2C{-}OH + 2C_2H_5ONa \qquad (2a)\\ \downarrow\\ (C_6H_5)_2CO + (C_6H_5)_2CHOH \qquad (2b)\end{array}$$

The sodium attaches itself to the ketone and gives the sodium ketyl which associates to sodium pinacolate with which it establishes an equilibrium; the ketyl is converted by the alcohol into a mixture of benzohydrol and benzophenone; the ketone that is regenerated in this manner then in its turn goes through the cycle of reactions until benzohydrol is the sole product. Benzopinacol may be formed by reaction of the sodium pinacolate with alcohol, but since the reaction is reversible the pinacol, like the ketyls will ultimately be converted rapidly to ketone and hydrol.[1]

If this mechanism be correct, then it should be possible to effect complete reduction by using only as much alcohol as is required by the formulation, since no loss of reducing agent occurs through evolution of hydrogen. This was found to be the case when the reduction was carried out in a mix-

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[1] Bachmann, THIS JOURNAL, *66,355* (1933).

ture of ether and benzene. Rapid and complete reduction takes place if a mixture of benzophenone and the theoretical amount of alcohol is shaken with 2% sodium amalgam in ether and benzene. Under these conditions it becomes even more apparent that the reduction proceeds through the intermediate formation of ketyl radicals, since the color phenomena are more pronounced; the solution becomes opaque dark blue and remains so until the end of the reaction when the solution becomes nearly colorless. The reaction is similar to the reduction of benzophenone by an equivalent amount of benzohydrol and sodium amalgam.[1] As a matter of fact, it was found that complete reduction can be effected by using only one-half the amount of alcohol required in the formulation since the benzohydrol can react in the manner of the alcohol.

In further support of this mechanism may be cited the fact that the identical results are obtained if the two reactions (Equations 1 and 2) are carried out separately in succession. This is accomplished by allowing the benzophenone to react with sodium amalgam in a mixture of ether and benzene in the absence of alcohol; in this way the reaction represented in Equation 1 takes place. If alcohol is added to this blue reaction mixture, then the reaction represented by Equation 2 occurs; after being shaken for a short time the mixture gives a quantitative yield of benzohydrol.

Similarly to benzophenone, other aromatic ketones can be reduced nearly quantitatively to hydrols in ether and benzene by sodium amalgam and a small amount of alcohol. Indeed, the procedure has proved to be an excellent practical method for preparing hydrols, possessing certain advantages over other methods of preparation. In support of our theory of the mechanism of reduction it was found that in every case the solution becomes deeply colored, and the color corresponds with the color characteristic of the individual sodium ketyl. Investigation has shown that the excellent method of Fosse[2] for the reduction of xanthone to xanthydrol by sodium amalgam and alcohol depends upon the intermediate formation of the xanthone-sodium compound. We have confirmed Fosse's observation that a blue color is developed during the reaction and we have found that the color is the same as that of the ketyl formed by the action of sodium amalgam on xanthone in absence of alcohol.

Various investigators have postulated the formation of intermediates in reductions. Cohen[3] considered that pinacols are formed by association of two diphenylhydroxymethyl radicals, $(C_6H_5)_2C$-OH, formed as intermediates by addition of an atom of hydrogen to benzophenone. He believed that pinacols are initially formed in the reduction of ketones to hydrols, and then broken down by the alkali. Willstätter, Seitz and

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(2) Fosse, Ann. chim., [9] 6, 58 (1916). See also "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 88.

(3) Cohen, *Rec. trav. chim*, 38, 72, 113 (1919).

Bumm[4] recently pointed out that the mechanism by which reduction by sodium amalgam takes place is still obscure. These investigators found that although pure sodium amalgam liberates no hydrogen from water, nevertheless reduction by this system is rapid. From their study of the reduction of terephthalic acid by sodium amalgam and water under various conditions, they came to the conclusion that the initial step consists in an addition of sodium to the atoms having free affinity.

Reduction of benzophenone by lithium amalgam and by potassium amalgam and alcohol follows the same course taken by sodium amalgam. In the reactions the intense blue colors of $(C_6H_5)_2C\text{-}OLi$ and of $(C_6H_5)_2C\text{-}OK$ are present until reduction of the ketone is complete; the yields of benzohydrol are quantitative.

Preliminary experiments with aliphatic ketones, with aldehydes, and with other compounds indicate that in many cases reduction by sodium amalgam and alcohol takes place through the intermediate formation of sodium addition derivatives. The results of these investigations will appear in future communications.

Experimental

Preparation of Sodium Amalgam.—Although many methods have been devised for preparing sodium amalgam, the following procedure proved to be most convenient for preparing 2% sodium amalgam rapidly in amounts necessary for our experiments. Sixty grams of mercury and 15 cc. of toluene are heated to the boiling point of the liquid in a 60-cc. Pyrex test-tube. One and two-tenths grams of sodium is cut into about a dozen pieces and added in portions to the hot mixture, shaking after each addition until reaction is complete. When all of the sodium has been added, the amalgam is cooled with shaking in order to prevent the amalgam adhering to the tube. The toluene is decanted from the solid amalgam and the latter is then removed from the tube, wiped clean with a cloth and broken into pieces.

Reduction of Benzophenone by Sodium Amalgam and Alcohol.—When a mixture of 60 g. of 2% sodium amalgam and 60 cc. of absolute alcohol was shaken, less than 1 cc. of hydrogen was evolved in the course of one hour. As soon as 3.64 g. of benzophenone was added and the mixture was shaken, a vigorous reaction ensued; the solid amalgam became liquid and heat was evolved, making it necessary to cool the flask. On being shaken vigorously the solution became blue; when shaking was stopped the blue color rapidly disappeared. Hydrolysis after one-half hour gave 3.56 g. (96%) of benzohydrol. When reduction by 40% sodium amalgam and alcohol was tried, a vigorous evolution of hydrogen occurred and the product was an oil that did not crystallize. Linnemann[5] obtained a 60% yield of benzohydrol by reducing benzophenone by solid sodium amalgam and 90% alcohol. Klages and Allendorff[6] found that benzophenone was reduced to diphenylmethane to the extent of 90% by the action of sodium and alcohol.

Reduction of Benzophenone in Ether and Benzene.—To 60 g. of 2% sodium amalgam in a 50-cc. cylinder or 50-cc. Erlenmeyer flask was added 25 cc. of anhydrous ether, 25 cc. of dry benzene and 2.5 cc. of absolute alcohol and finally 3.64 g. (0 02 mole) of

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[4] Willstätter, Seitz and Bumm, *Ber.*, **61B**, 871 (1928)

[5] Linnemann, Ann, 163, 6 (1865).

[6] Klages and Allendorff, Ber., 31, 998 (1898).

benzophenone. The tube was corked and shaken. Almost immediately the solution became dark blue in color; it was necessary to cool the flask. After five minutes the solution was opaque blue; after ten minutes the color was less intense and after fifteen minutes the solution was transparent pale green. At the end of this time the mixture was poured into water contained in a separatory funnel, the mercury was drawn off and the solution was acidified. The ether–benzene solution was separated and evaporated; the residue was nearly pure benzohydrol. After recrystallization from petroleum ether the benzohydrol weighed 3.60 g. (98%).

Reduction of Other Ketones.—In Table I are given the results obtained by reducing a number of representative aromatic ketones, following the procedure described for benzophenone. In each case 0.2 gram-moie of ketone, 60 g of 2% sodium amalgam and 2.5 cc of absolute alcohol was shaken in 50 cc. of a mixture of ether and benzene. The mixtures were hydrolyzed as soon as the solution had only a pale color, which generally occurred in fifteen to thirty minutes. The yields given in the table are based on recrystallized product. Phenyl a-naphthyl ketone gave a number of products; this ketone is being studied further.

TABLE I

REDUCTION OF AROMATIC KETONES TO HYDROLS BY SODIUM AMALGAM AND ALCOHOL

Ketone	*Color during reduction*	Hydrol yield, %
Benzophenone	Blue	98
4-Methylbenzophenone	Blue	98
4,4'-Dimethylbenzophenone	Blue	96
4-Phenylbenzophenone	Green	98
4,4'-Diphenylbenzophenone	Green	99
Fluorenone	Brown-green	99

4,4'-Diphenylbenzophenone and 4,4'-Diphenylbenzohydrol.—We have found that the method of Adam' for preparing 4.4'-diphenylbenzophenone from biphenyl and phosgene in the presence of aluminum chloride gives excellent yields of the ketone. Because of the difficulty involved in obtaining phosgene on account of shipping regulations, a different method was devised Staudinger[8] found that oxalyl chloride and benzene react and give henzophenone and we have now applied the reaction to oxalyl chloride and biphenyl. A mixture of 70 g. of oxalyl chloride, 200 g. of biphenyl and 150 cc. of carbon disulfide was warmed to 40–50° in a I-liter round-bottomed flask fitted with a reflux condenser. To the mixture 100 g. of anhydrous aluminum chloride was added in portions at such a rate as to keep the mixture boiling. After addition was complete the mixture was warmed for one hour on a steam-bath and was then allowed to stand overnight. The hydrolyzed mixture was warmed on a steam-bath in order to remove the carbon disulfide and the solid diphenylbenzophenone was filtered off, washed and dried. In order to remove biphenyl, the crude ketone was warmed with a large amount of alcohol and the mixture was filtered while hot. The ketone was obtained in the form of colorless leaflets by extracting it in a Soxhlet extractor with a mixture of equal parts of acetone and benzene; extraction took place at the rate of *2* g. of ketone per hour; yield, 155 g. (80%) ; m. p. 233°. Contrary to statements in the literature the ketone is very little soluble in hot alcohol or in hot benzene.

It is difficult to reduce 4,4'-diphenylbenzophenone by many reducing agents because of the insolubility of the ketone in most solvents. By our procedure the carbinol is prepared in quantitative yields. In one experiment 33.4 g. (0.1 mole) of diphenylbenzophenone was added to 300 g. of 2% sodium amalgam and 12.5 cc. of absolute

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(7) *Adam, Ann. chim. phys.*, [6] 16, 258 (1888)

(8) *Staudinger, Ber.*, *41*, 3563 (1908).

alcohol in 150 cc. of ether and 150 cc. of benzene The mixture was warmed to 40°, stoppered and shaken. The reaction was slow until the amalgam became liquid (two hours); then on being shaken vigorously so that the amalgam was dispersed into fine globules the mixture became dark green and all of the ketone was reduced in five minutes. The diphenylcarbinol which was obtained by hydrolysis of the nearly colorless solution was recrystallized from acetone (3.5 cc. of acetone per gram of carbinol) and was obtained in the form of large colorless needles; yield, 33 g.; m. p. 151–152°.

Reduction of the System, Sodium Ketyl $\rightleftharpoons$ Sodium Pinacolate.—A mixture of 3.64 g. of benzophenone and 60 g. of 2% sodium amalgam in ether and benzene was shaken for two days. To the blue mixture of sodium ketyl and sodium pinacolate was added 2.5 cc. of absolute alcohol and the resulting mixture was shaken for fifteen minutes. Hydrolysis gave a quantitative yield of benzohydrol. In like manner the ketyl-pinacolate mixtures obtained from 4-phenylbenzophenone and 4.4'-diphenylbenzophenone were reduced completely to the hydrol.

Reduction of Benzophenone by Lithium Amalgam and by Potassium Amalgam.—Lithium amalgam was prepared by keeping 0.35 g. of lithium, cut into several pieces, under 60 g. of heated mercury covered with toluene; several hours were often required for complete combination. The semi-solid amalgam was cleaned and added to a solution of 3.64 g. of benzophenone and 2.11 cc. of alcohol in 60 cc. of ether and benzene. The solution became dark blue in color; after being shaken for fifteen minutes the solution was nearly colorless. Hydrolysis gave a quantitative yield of benzohydrol.

In like manner an intense blue color resulted when 1.82 g. of benzophenone in ether and benzene was shaken with 1.3 cc. of alcohol and potassium amalgam that had been prepared from 0.88 g. of potassium and 50 g. of mercury. After half an hour little color remained; hydrolysis gave a quantitative yield of benzohydrol.

Summary

Benzophenone and a number of other aromatic ketones are reduced in ether–benzene solution quantitatively to hydrols by 2% sodium amalgam and a small amount of alcohol.

The reduction of ketones to hydrols by 2% sodium amalgam and alcohol is not effected by hydrogen liberated by the action of the amalgam on the alcohol. It has been shown that the reduction proceeds through the intermediate formation of ketyl radicals: (a) $2(C_6H_5)_2CO + 2Na \longrightarrow 2(C_6H_5)_2CONa \rightleftharpoons (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2$; (b) $2(C_6H_5)_2CONa + 2C_2H_5OH \longrightarrow (C_6H_5)_2CHOH + (C_6H_5)_2CO + 2C_2H_5ONa$. The ketone that is regenerated in this manner goes through the series of reactions until the hydrol is the sole product.

A study is being made of the mechanism of reduction of other types of ketones and of other compounds.

ANN ARBOR, MICHIGAN

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

Cyclic and Polymeric Compounds from the Reactions of Ethylene Mercaptan with Polymethylene Halides

BY N. BEVERLEY TUCKER AND E. EMMET REID

Recently there has been much interest in the formation of cyclic and "string" molecules by the interaction of bifunctional compounds. Staudinger and his co-workers[1] have considered such reactions in relation to high polymers while Carothers[2] has elaborated the theory for the reactions of bifunctional compounds in general and with the aid of several co-workers[3] has verified his conclusions by studies of the esters of various α,ω-glycols with α,ω-dibasic acids. The data so obtained are important for an understanding of the formation of rings and for the theories of strainless rings as well as for an understanding of high polymers.

The reactions of dimercaptans with dihalides offer the same possibilities as those of other bifunctional molecules and may be expected to show, in addition, some of the peculiarities of sulfur compounds. The possible reactions can be illustrated with sodium ethylene mercaptide (I) and ethylene bromide (II). Since it is highly improbable that both of the reactive groups of the one molecule will come into contact with both of those of the other molecule simultaneously, it is sufficient to consider only the reactions in which one group of each takes part.

$$\mathrm{NaSCH_2CH_2SNa(I) + BrCH_2CH_2Br(II) \longrightarrow NaSCH_2CH_2SCH_2CH_2Br(III)} \quad (1)$$
$$\mathrm{I + III \longrightarrow NaSCH_2CH_2SCH_2CH_2SCH_2CH_2SNa\ (IV)} \quad (2)$$
$$\mathrm{II + III \longrightarrow BrCH_2CH_2SCH_2CH_2SCH_2CH_2Br(V)} \quad (3)$$
$$\mathrm{IV + II \longrightarrow NaSCH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2Br(VI)} \quad (4)$$

The reaction of I with V also gives VI. In the preparation of ethylene mercaptan both Meyer[4] and Râ̂y[5] have found high boiling liquids, one of which Râ̂y identified as $\mathrm{HSCH_2CH_2SCH_2CH_2SCH_2CH_2SH(IVa)}$, which corresponds to IV above. The presence of other members of this series has been suggested by V. Meyer.

There is no obvious reason why these processes should not continue indefinitely, since VI may react with I or with II and every product that is formed has reactive groups at both ends. Whether bromine atoms, as in V, or —SNa groups, as in IV, predominate will depend on the relative proportions of the original reactants. It is to be noted that the products are of two kinds, those such as IV and V which have the same kind of groups at both ends and those like III and VI which have different groups

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(1) Staudinger, *Ber.*, **59**, 3019 (1926); and other articles too numerous to list.

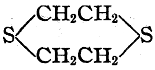
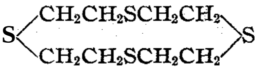
(2) Carothers, THIS JOURNAL, **51**, 2548 (1929); *Chem. Rev.*, **8**, 353 (1931).

(3) THIS JOURNAL, **51**, 2560 (1929); **52**, 314, 711, 3292 (1930); **54**, 1559, 1566, 1569 and 1579 (1932).

(4) Meyer, *Ber.*, **19**, 3259 (1886).

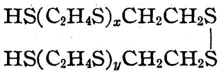
(5) Râ̂y, *J. Ind. Chem. Soc.*, **6**, 865 (1929).

at the two ends and are thus capable of reacting intramolecularly to form ring compounds such as


(VII) and

(VIII)

It is evident that reactions such as these may go on in the preparation of all the polymethylene mercaptans by the usual reactions of the polymethylene bromides on sodium hydrosulfide, since the dimercaptans are present with the dibromides during the course of the reaction. There is here the additional possibility that compounds III, V and VI may react with sodium hydrosulfide which is present in abundance to give a complete series of sulfide–dimercaptans like IV. It is well known that the yields of the polymethylene mercaptans are usually not large and that considerable amounts of amorphous polymeric materials are obtained as by-products.

It has been observed that the high boiling liquids mentioned above are readily oxidized by air to form high molecular weight products. Little is known of these and it may be assumed that some are linear and some cyclic.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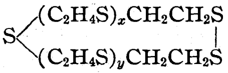
(X)

A relatively high proportion of disulfide linkages in the molecule will be evidenced by a high sulfur content.

While rings of any size are possible, from what we know of the arrangement of molecules in space it appears to be very unlikely that the terminal groups will be near enough together for ring closure except when the chains are of certain lengths. It is well known that the reaction of ethylene bromide and sodium sulfide gives 1,4-dithiane along with polymers. Dithiane and polymers are also obtained as by-products in the preparation of ethylene mercaptan. Thus ring closure takes place readily at the stage III to form a six-membered ring. Râу[5,6] has reported a trimeric ring of ethylene sulfide but Bennett and Berry[7] could not get this. Dithiane is the only ring compound that we have isolated from the above reactants. It is quite possible that larger rings of various sizes are mixed with the string molecules in the high molecular weight, insoluble materials that are obtained from such reactions. Mansfeld[8] obtained 1,3,5-trithiane, which is also a six-membered ring, from methylene iodide and sodium sulfide.

From the time of Crafts[9] in 1862 reactions of this type have been studied and many facts have been accumulated but there are many gaps and some discrepancies in the recorded information. The purpose of the present study was to coordinate and extend the earlier observations. It consists of

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(6) Râу, J. Chem. *Soc.*, **117**, 1090 (1920); **121**, 1279 (1923); **123**, 2174 (1923).

(7) Bennett and Berry, *ibid.*, 127, 910 (1925).

(8) Mansfeld, *Ber.*, **19**, 697 (1886).

(9) Crafts, Ann., 124, 112 (1862)

three parts: (I) the isolation of cyclic molecules from reactions between sodium ethylene dimercaptide and the methylene and polymethylene halides up to the hexa-, (2) study of the polymers, particularly those formed in the preparation of ethylene mercaptan, (3) depolymerization or decomposition of some of the more complex compounds.

Ring Formation

The results of our work are given in Table I. In all cases ethylene mercaptan reacted with the dihalide in the presence of alkali. In some cases both the monomeric and the dimeric rings have been obtained while in others only the one or the other. It will be noted that those containing 5, 6 and 7 members are obtained in considerable yields while the monomeric 8 and 9 rings could not be isolated and the 10 was found in only small amount. All of the preparations were made under the conditions found best for 1,4-dithiane. Small yields of dimeric rings of 10, 14, 16 and 18 members were obtained.

The ring No. 1, 1,3-dithiolane was made by Gibson[10] and previously by Baumann and Walter.[11] Gibson gives the sulfone as melting at 224°, which he says checks with the results of previous workers who gave 204–205°. The sulfone from our product melted at 204.5–205°.

TABLE I

RINGS FORMED FROM ETHYLENE MERCAPTAN AND POLYMETHYLENE DIHALIDES

No.	Dihalide	Ring formed	Atoms	Yield, %	M. p., °C.	Molecular wt. Calcd.	Molecular wt. Found
1	CH_2Cl_2	$(CH_2)_2S_2CH_2$	5	26	−51	106	109
2	CH_2Cl_2	$[(CH_2)_2S_2CH_2]_2$	10	0.2	121	212	219
3	$(CH_2)_2Br_2$	$(CH_2)_2S_2(CH_2)_2$	6	46	111	120	118
4	$(CH_2)_3Br_2$	$(CH_2)_2S_2(CH_2)_3$	7	9	47.0	134	140
5	$(CH_2)_3Br_2$	$[(CH_2)_2S_2(CH_2)_3]_2$	14	1	122	268	247
6	$(CH_2)_4Br_2$	$[(CH_2)_2S_2(CH_2)_4]_2$	16	0.2	73	296	290
7	$(CH_2)_5Br_2$	$[(CH_2)_2S_2(CH_2)_5]_2$	18	.15	89	324	319
8	$(CH_2)_6Br_2$	$(CH_2)_2S_2(CH_2)_6$	10	.06	65	176	240

The yield of dithiane was better at room temperature than at the boiling temperature of the alcoholic solution.

The ring No. 4 was prepared from trimethylene mercaptan and ethylene bromide but not isolated by Autenrieth and Wolff,[12] who gave 282° as the melting point of its sulfone, which agrees with ours. Ring No. 5 has not been isolated previously.

Rings Nos. 6, 7 and 8 were obtained only in minute yields and on this account the statements about them are to be regarded as preliminary only. They separate in crystals when the ether extracts of the accompanying polymers are evaporated to small volume. They were recrystallized from

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(10) Gibson, J. Chem Soc , 1930, 13.

(11) Baumann and Walter, *Ber.*, 26, 1129 (1893).

(12) Autenrieth and Wolff, *ibid.*, 32 (1899).

ether and alcohol. It is noteworthy that the monomeric 8 and 9 membered rings were not obtained.

Polymers

In the preparation of all of the ring compounds of Table I, large amounts of polymers were obtained. In appearance they are all much alike, white, fluffy and apparently amorphous. Their sulfur content is in all cases within 1% of that of the rings which they accompany. This suggests chains made up of the unit $—(CH_2)_2—S—(CH_2)_n—S—$. In case the bromide is in excess one or both of the terminal groups may be bromine atoms as seems to have been the case in the polymers studied by Rây and Bose-Rây.[13]

Bennett and Hill[14] suggest $—CH{=}CH_2$ and $—CH_2OH$ as possible end groups. It seems more likely that $—OC_2H_5$ may be formed occasionally by the reaction of the bromide with sodium ethylate, a trace of which must be present in the reaction mixture.

All of these polymers are mixtures which can be roughly separated into fractions by partial solution in solvents such as ether, benzene and chloroform. The solubility in chloroform increases as the number of carbons in the polymethylene bromide goes up.

The mixture of polymers obtained in the preparation of ethylene mercaptan was studied more extensively on account of its availability. Indications as to the nature of these are obtained from a consideration of the products intermediate between the ethylene mercaptan and the solids. Steam distillation of the ethylene mercaptan leaves a quantity of heavy oil a part of which is slightly volatile with steam. A quantity of this oil was collected and fractionated but sharp cuts could not be obtained. A portion boiling at 120–140° at 30 mm. from which dithiane crystallized showed an average molecular weight of 154 corresponding to $HSC_2H_4SC_2H_4SH$. Iodine titration gave the high equivalent weight of 132, which was probably due to the presence of dithiane. This oil on standing for several days precipitated an amorphous white solid entirely similar to the original polymeric part. An iodine titration of the remaining oil gave an equivalent weight of 151, showing that it had suffered oxidation. In a portion of the original oil that had been steam distilled a white solid appeared after a time. This was filtered off and freed from dithiane by washing with ether and showed a molecular weight of 1300. It was no longer volatile with steam. It must have been formed by spontaneous oxidation.

The solid polymers from several preparations were united and separated roughly into fractions by successive extractions with solvents. The properties of these are shown in Table II.

No. 5 was titrated with iodine and gave 2950 and 3000 as equivalent

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(13) Rây and Bose-Rây, J. Indian *Chcm. Soc.*, **3**, 75 (1928).

(14) Bennett and Hill, J. *Chem. Soc.*, 1803 (1927).

TABLE II

PROPERTIES OF THE FRACTIONS OF THE POLYMERS

No.	Solvent	Wt.	Softens at °C.	Melts at °C.	S, %		Mol. wt	
1	Ether	...	..	30–40				
2	Benzene	2.6	..	80–83	59.5	59.7	1330	1380
3	Hot benzene	8.0	74	79–81	65 8	64.1	1750	1690
4	Hot benzene	1.4	58	67–72	04.2	64.7	1530	1350
5	Hot chloroform	13 0	70	80–81	63.0	62 6	2880	
6	Hot benzene	4.5	66	79–84	63.0	62.6	2325	2660
7	Hot benzene	3.5	67	80–82	61.8	51.3	1366	1388
8	Hot xylene	4.0	65	88–91	62.0			
9	Hot nitrobenzene	2.4	86	118–121	64.2			

weights. Bromine was not detected in any of the fractions. Fraction No. 1 was waxy. It is to be noted that all of the fractions show a higher sulfur content than the unit —CH_2CH_2S—, which has 53.3%. The molecular weight and composition of No. 5 would be accounted for by $(C_2H_4S)_{38}S_{18}$, indicating a large number of disulfide linkages. This approximates (—$CH_2CH_2SCH_2CH_2S$—S)$_{18}$, an oxidation product of $HSCH_2CH_2SCH_2CH_2SH$.

On account of the amorphous character of the polymers, x-ray inspection[15] did not show much but powder diagrams of all of the fractions showed the spacing —C—C—S—. Nos. 2, 4 and 9 were photographed with a larger camera and Nos. 4 and 9 gave a line corresponding to —C—C—S—S—.

Depolymerization

Apparently these polymers show no reaction corresponding to the ester interchange found by Carothers.[16] Dithiane heated for two days in a sealed tube to 180–190° was unchanged. The polymers heated for several hours in a molecular still under high vacuum showed no decomposition. In some cases there was a slight sublimation of low molecular weight material which was probably present originally.

Bennett[17] has shown that ethylene sulfide polymers give dithiane on heating with ethylene bromide. The reaction involves the formation of a sulfonium bromide since ionic bromine appears. We have extended this reaction to all of our polymers and have obtained dithiane from all of them. The yields are given in Table III. The same polymers heated with trimethylene bromide do not yield any isolable ring compounds though ionic bromine is formed. This is curious considering the fact that the ring $(CH_2)_2S_2(CH_2)_3$ is readily obtained from ethylene mercaptan and trimethylene bromide. These facts are further evidence of the unique properties of six-membered rings.

(15) For which our thanks are due to Mr. D. A Wilson.

(16) Carothers, THIS JOURNAL, 54, 761 (1932).

(17) Bennett, *J. Chem. Soc.*, 1803 (1927)

TABLE III

YIELDS OF DITHIANE FROM POLYMERS WITH ETHYLENE BROMIDE

Polymer	Percentage of weight	Percentage of calcd.
$[-CH_2S(CH_2)_2S-]_x$	51	43
$[-(CH_2)_2S(CH_2)_2S-]_x$	65	65
No 2 Table II	28	32
No. 9 Table II	24	31
$[-(CH_2)_2S(CH_2)_3S-]_x$	25	28
$[-(CH_2)_2S(CH_2)_6S-]_x$	21	31

To get further light on this reaction by applying it to a compound of known structure, dibutyl dithioglycol ether, $C_4H_9SCH_2CH_2SC_4H_9$, was prepared and heated with ethylene bromide. A 48% yield of dithiane was obtained but a similar experiment using trimethylene bromide gave no definite results.

It was found that some of the polymers give dithiane when heated in a current of hydrogen chloride. The results of this treatment are given in Table IV.

TABLE IV

YIELDS OF DITHIANE FROM POLYMERS WITH HYDROGEN CHLORIDE

Polymer	Percentage of weight	Percentage of calcd.
$[-(CH_2)_2S(CH_2)_2S-]_x$	40	40
$[-(CH_2)_2S(CH_2)_3S-]_x$	18	40
$[-(CH_2)_2S(CH_2)_6S-]_x$	14	41

The polymer $[-CH_2S(CH_2)_2S-]_x$ gave a 30% yield of the corresponding monomeric ring, 1,3-dithiolane.

Experimental

Ethylene mercaptan was prepared by heating for one and a half hours in an autoclave at about 100° with stirring, ethylene chloride and a 10% excess of aqueous sodium hydrosulfide made by saturating crystalline sodium sulfide, $Na_2S \cdot 9H_2O$, with hydrogen sulfide. The pressure developed was about 2.5 atm. The product was acidified with sulfuric acid and the mercaptan distilled out with steam. The crude mercaptan was dried and fractionated in a column still, b. p. 146–146.5°. It melted at −41 to −41.4" and had n_D^{25} 1.5558. The yields were 55 to 65%.

Trimethylene and pentamethylene bromides were purchased from the Eastman Kodak Co. The tetra- and hexamethylene bromides were prepared from the corresponding glycols which were obtained by the Beauveault and Blanc reduction of the butyl esters of succinic and adipic acids.

The condensations of ethylene mercaptan with the polymethylene bromides were all carried out in the same way: 0.25 mole of the mercaptan was dissolved in 500 cc. of absolute alcohol in which 12 g. of sodium had been dissolved and 0.25 mole of the bromide added slowly at room temperature. The separation of sodium bromide began immediately but the mixture was boiled for one-half hour and poured into water. Ether was added and the whole filtered. The solid material was dried and extracted for twelve hours with ether. The two ether solutions were united and dried over calcium chloride and evaporated to get the monomeric and dimeric ring compounds.

1,3-Dithiolane.—The evaporation of the ether solution obtained as above left 10 g. of oil which was distilled, 7 g. going over between 178 and 182" or 26%. This was fractionated through a small column and gave 5 g. boiling at 179–180°. This had n_D^{25} 1.5983 and solidified at −51 to −52°; molecular weight in borneol, 108, 110; calcd., 106. The residue from the distillation was a heavy oil from which needles separated after three weeks standing. These were picked out, dried on filter paper and recrystallized twice from ether and once from alcohol; yield, 50 mg., 0.2%, m. p. 121°, mol. wt. calcd. 212; found 220; sulfur calcd., $C_6H_{12}S_4$, 60.3; found, 63.3.

Dithiane.—The experimental conditions given above were chosen after a number of experiments on the condensation of ethylene mercaptan with ethylene bromide. Where the reaction was run at the boiling temperature the ratio of polymer to dithiane was 2:1 but at room temperature the yield of dithiane was 46% to 51 of polymer. At 0° the ratio was even more favorable to dithiane but the reaction was incomplete.

Ethylene-trimethylene Disulfide.—On evaporation of the ether extracts some amorphous material separated and later small colorless apparently cubic crystals, weight 0.15 g. These were unaffected by alkali, gave no test for halogen, melted at 121–122°; m. w. calcd. for $C_{10}H_{20}S_4$, 268; found, 247; sulfur calcd., 47.8; found, 48.1. Complete evaporation of the ether left a yellow semi-crystalline mass from which flakes were obtained by sublimation on the water-bath, yield 3.2 g. or 9%. These melted at 47.0–47.5° and contained 47.4, 48.0% of sulfur; calcd. for $C_5H_{10}S_2$, 47.8; m. w. 140; calcd., 134. The sulfone was obtained by oxidation of 0.3 g. suspended in 20 cc. of water by the addition of potassium permanganate and acid, m. p. 281–282°.

Ethylene-tetramethylene Disulfide.—This was prepared in a slightly different way. A slight excess of 50% caustic soda was added dropwise to a solution of 11 g. of the dibromide and 5 g. of the mercaptan in 150 cc. of alcohol. The mixture was heated for thirty minutes, poured into water and extracted with ether. Crystals separate from the ether.

Ethylene-pentamethylene Disulfide.—This was obtained in the same way as the above.

Ethylene-hexamethylene Disulfide.—In this case the ether solution deposited amorphous material along with a small amount of crystals. These were picked out and recrystallized from ether.

Summary

Ethylene mercaptan has reacted with methylene chloride and the polymethylene bromides up to the hexa-. Cyclic compounds have been obtained in all cases along with amorphous materials having high molecular weights.

All of the polymers give dithiane when heated with ethylene bromide. The most of them give the same material when heated in a current of dry hydrogen chloride.

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The Reaction of Iodine Monochloride with Certain Organic Mercury Compounds

BY FRANK C. WHITMORE AND M. A. THORPE[1]

Although the reaction with iodine is one of the oldest and most widely used reactions of organic mercury compounds,[2] the analogous reaction with iodine monochloride has been neglected. The literature contains only one reference to it, namely, the action of iodine chloride with mercurated camphors to give diiodocamphor.[3]

The present study was undertaken to determine whether iodides or mixtures of iodides and chlorides are formed and to determine the feasibility of using iodine monochloride in place of iodine for the preparation of iodo compounds from organic mercury compounds.[4] The mercury compounds studied correspond to the various parts of Kharasch's table of "relative electronegativity."[5] The mercury compounds selected contained the groups, #-anisyl-, @-naphthyl-,#-tolyl-, phenyl- and @-phenylethyl-. In all except the last, yields of over 90% of the iodo compounds were obtained. No trace of organic chloro compound was detected. Phenylethylmercuric chloride gave a mixture of phenylethyl iodide and phenylethyl chloride. The latter was probably formed by the action of iodine chloride on the phenylethyl iodide. This is like the action of ethyl iodide with iodine monochloride.[6]

The solvent had a marked effect on the reaction of iodine monochloride with the organic mercury compounds. In general, water was the best medium for the reactions in spite of the extreme insolubility of the mercury compounds in it.

Experimental

Iodine monochloride was prepared directly from the elements.[7]

In studying solvents for use with the iodine monochloride it was observed that widely varying heats of solution were given with different solvents. In experiments under essentially identical conditions the addition of 1 cc. of iodine monochloride to 25 cc. of solvent at 25° gave the following rises in temperature in degrees centigrade: ethylene chloride, 0.2; chlorobenzene, 0.6; distilled water, 2.0; benzene (*c. p.*), 2.1; acetic acid (glacial), 2.7; hydrochloric acid (*c. p.*), 3.3; ether (anhydrous), 5.0; ether (U. S. P.), 5.9; ethanol (absolute), 7.5; ethanol (95%), 5.3; chloroform, −1.3; carbon

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(1) Presented in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

(2) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., N. Y., 1921, pp. 67–73.

(3) Marsh, J. *Chem. Soc.*, 97, 2413 (1910).

(4) Cf. Whitmore and Hanson, "Organic Syntheses," 1925, Vol. V, p. 37.

(5) Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

(6) Friedel and Silva, Bull. *soc. chim.*, [2] 17, 532 (1871).

(7) Jackson and Whitmore, THIS JOURNAL, 37, 1528 (1915).

tetrachloride, −2.7. Each of these figures is the average of several determinations. The results are given merely as an indication of phenomena which should perhaps be studied with greater refinement.

***p*-Anisylmercury Compounds.**—*p*-Bromoanisole, b. p. 215–217°, was prepared in 88% yield from anisole and phosphorus pentabromide. The bromo compound was converted to di-p-anisylmercury, m. p. 200–202°, in 48% yield by treatment with 3% sodium amalgam.[8]

Action of Iodine Monochloride with **Di-*p*-anisylmercury.** **(a)** In Carbon Tetrachloride.—A solution of 8.3 g. (2 mols) of iodine monochloride in 100 cc. of dry carbon tetrachloride was added with stirring during two hours to a suspension of 10.7 *g.* (1 mol) of di-p-anisylmercury in 250 cc. of the same solvent. The mercuric chloride was filtered off and the solution was shaken with sodium thiosulfate solution to remove a trace of free iodine. The solution was washed with water and the excess solvent removed by distillation. The residue crystallized giving 11.5 g. of p-iodoanisole, m. p. 50–51°, a yield of 95%. The melting point of the pure substance is given as 51–52°.

(b) In Water.—Iodine monochloride (8.3 g., 2 mols) was added with stirring during three hours to a suspension of 10.7 g. (1 mol) of the mercury compound in 100 cc. of water boiling under a reflux condenser. The mixture was cooled to 60° and treated with 50 cc. of carbon tetrachloride, separated and washed with several 20-cc. portions of the solvent. The carbon tetrachloride solution was worked up as before to give 12.1 g. of crude p-iodoanisole. Crystallization from 100 cc. of 95% alcohol gave 11.5 g. of the pure substance, m. p. 50–51°.

Action of Iodine Monochloride with ***p*-Anisylmercuric** Chloride.—The mercury compound was made from mercuric chloride and the mercury-bis compound in boiling alcohol in the usual way (Ref. 2, p. 65).

A solution of 1.3 g. (1 mol) of iodine monochloride in 50 cc. of carbon tetrachloride was added slowly with stirring to a suspension of 2.6 g. (1 mol) of *p*-anisylmercuric chloride in 50 cc. of the solvent. The product was 1.7 g. of p-iodoanisole, m. p. 50–51°, a yield of 95%.

β-Naphthylmercuric Chloride.—The mercury compound, m. p. 237–238°, was made from β-naphthylamine in 60% yield.[9] A solution of 5.6 g. (1 mol) of iodine monochloride in 50 cc. of 95% alcohol was added during three hours with stirring to a refluxing suspension of 12 g. (1 mol) of @-naphthylmercurichloride in 100 cc. of the same solvent. The clear solution was evaporated to half its volume under reduced pressure and then was allowed to evaporate spontaneously. The residue was slightly yellow and contained a few very small red crystals. It was washed with 150 cc. of water to remove mercuric chloride. The pale yellow residue was dried in a desiccator and crystallized twice from 50 cc. of absolute ethyl alcohol. The resulting β-iodonaphthalene, m. p. 53–54", weighed 8.0 *g.*, a yield of 95%. The pure substance melts at 54.5°.

***p*-Tolylmercuric** Chloride.—The mercury compound, m. p. 230–232°, was prepared from p-toluene sulfonyl chloride.[10] The experiments with this substance are summarized in Table I. In each case the iodine monochloride or its solution was added to the mercury compound with efficient stirring.

Diphenylmercury.—This was prepared from bromobenzene and 3% sodium amalgam.[11] (a) In carbon tetrachloride. A solution of 32.4 g. (2 mols) of iodine monochloride in 100 cc. of carbon tetrachloride was added during four hours with stirring to a suspension of 35.4 *g.* (1 mol) of diphenylmercury in 200 cc. of the same solvent at room temperature. The mixture was worked up in the usual way, the product being dried

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(8) Cf. Michaelis and Rabinerson, Ber., 23, 2343 (1890).

(9) Nesmajanow, "Organic Syntheses," 1932, Vol. XII, p. 54

(10) Whitmore, Hamilton and Thurman, ibid., 1923, Vol. III, p. 99.

(11) Calvery, *ibid* , 1929, Vol IX, p 54.

TABLE I

ACTION OF *p*-TOLYLMERCURIC CHLORIDE WITH IODINE MONOCHLORIDE

Hg cpd., g.	Solvent	Cc.	ICl, g.	Solvent	Cc.	Temp., ° C.	Time	*p*-Iodotoluene, g.	M. p., ° C.	Yield, %
32.6	CCl_4	200	16.2	CCl_4	100	Boiling	2 days	13.5	33–35	50[a]
163	H_2O	400	81	None		Boiling	5 hrs.	90.5	33–34	87[b]
81.5	H_2O	200	39.6	Water (14.59 NaCl)	200	Boiling	5 hrs.	49	33.5–34.5	92
8	H_2O	100	4.0	Water (1.5 g. NaCl)	100	Boiling	4 hrs.	4.5	33–33.8	88
8	H_2O	100	4.0	Water (1.5 g. NaCl)	100	20	18 hrs.	2.4	30–32	50
16	H_2O	100	8.1	Concd. HCl	25	Boiling	4 hrs.	7.3	33–34	67
16	H_2O	100	8.1	Concd. HCl	15	Boiling	4 hrs.	7.3	33–34	67
16	H_2O	100	8.1	Water (15 g. NaI)	50	Boiling	4 hrs.	8.3	33–34	76
16	H_2O	100	8.1	Water (11 g. $CaCl_2$)	50	Boiling	4 hrs.	5.8	32–33	53
16	H_2O	100	8.1	Water (18 g. KI)	50	Boiling	1 hr.	9.5	34–35	87
8	Dry ether	100	4	Dry ether	50	20	2 hrs.	1.1		21
8	95% Alc.	100	4	Alcohol	50	20	2 hrs.	1.2		27
16	Glac. HOAc	150	8.1	Glacial acetic acid	50	Boiling	4 hrs.	6.3		58
16.3	H_2O	250	12.7 g. I	Water (12.7 g. KI)	50	Boiling	5 hrs.	10.1	34–35	92

[a] No *p*-chlorotoluene could be detected. [b] Allowing for 7.7 g. of unreacted mercury compound. There was also obtained 5 g. of an oil which solidified at 5°. No evidence of *p*-chlorotoluene was obtained.

by the addition of 60 cc. of dry benzene and then distilling. The residue boiling above 100° was carefully fractionated with a 30 X 0.7 cm. adiabatic total condensation variable take-off column[12] using a reflux ratio of 20:1. The properties of the pure substances which might be formed are as follows: chlorobenzene, b. p. 132°, n_D^{20} 1.525; iodobenzene, b. p. 188°, n_D^{20} 1.621. The distillation gave the following fractions (with b. p. at 735 mm., wts. and n_D^{20} as given): No. 1, 100–147°, 1.7 g., 1.502; No. 2, 147–182°, 2.8 g., 1.544; No. 3, 182–184°, 14.6 g., 1.617; No. 4, 184–185°, 17.2 g.; residue 2.1 g. Fractions 3–4 represent a 78% yield of iodobenzene. The above experiment was repeated but the carbon tetrachloride solution was dried and distilled directly. The same yield of iodobenzene, b. p. 181–185" and n_D^{20} 1.618 was obtained. (b) In water. This run was like that of di-*p*-anisylmercury. The fractionation of the product gave no material boiling under 175". The yield of iodobenzene, b. p. 182–185°, was 78%.

In order to test the efficiency of the fractionation, a mixture of 2.92 g. of chlorobenzene and 26.3 g. of iodobenzene was fractionated in the same way. The fractions (including b. p. at 736 mm., wt., and n_D^{20}) follow: No. 1, 130–137°, 1.4 g., 1.532; No. 2, 137–144°, 0.63 g., 1.539; No. 3, 144–152°, 0.55 g., 1.5452; No. 4, 152–162°, 0.50 g., 1.556; No. 5, 162–173°, 0.71 g., 1.578; No. 6, 173–183°, 4.3 g., 1.609; No. 7, 183–184°, 19.1 g., 1.620; residue, 1.4 g.; loss 0.59 g. The recovery of iodobenzene, b. p. 173–184°, was 89%.

β-Phenylethylmercuric Chloride.—Phenylethyl chloride, b. p. 81–84" (14 mm.), n_D^{20} 1.5294, was prepared in 87% yield by the action of thionyl chloride on the alcohol. The chloride was converted to the Grignard reagent which was then refluxed with mercuric chloride[13] to give an 85% yield of the mercury compound, m. p. 163–166°. When this product was recrystallized from alcohol and analyzed by decomposing with sulfuric acid and hydrogen peroxide and precipitating mercuric sulfide in the usual way, it gave results for mercury one per cent. low.

A solution of 35.6 g. (1 mol) of iodine monochloride in 20 cc. of carbon tetrachloride was added during five hours with stirring to a refluxing suspension of 75 g. (1 mol) of phenylmercuric chloride in 200 cc. of the same solvent. The process was interrupted in the middle and the mixture stood overnight at room temperature. The mixture was worked up as usual and the product was fractionated through the 30 X 0.7 cm. column at 14 mm. using a 15:1 reflux ratio. Six fractions were obtained amounting to 26.5 g. The chief fraction was No. 6, b. p. 107–115° (14 mm.), 15.5 g., n_D^{20} 1.597. Fraction 2, b. p. 83–85' (14 mm.), 4.7 g., n_D^{20} 1.533, contained 23.2% chlorine and Fraction 6 contained 54.5% iodine, indicating them to be nearly pure phenylethyl chloride and iodide, respectively. The yields of these two substances were about 35 and 30%.

Treatment of Phenylethyl Iodide with Mercuric Chloride.—A mixture of 15 g. (1 mol) of phenylethyl iodide and 17.5 g. (1 mol) of mercuric chloride in 100 cc. of carbon tetrachloride was refluxed with stirring for twelve hours. After standing for forty-eight hours a few red crystals were visible in the solid material. The mixture was worked up in the usual way and the product was fractionated to give 10.4 g. of unchanged phenylethyl iodide, b. p. 107–111° (13 mm.), n_D^{20} 1.595. The low boiling material was only 0.7 g. Its n_D^{20} was 1.555. Thus no phenylethyl chloride (b. p. 80–82.5° (13 mm.), n_D^{20} 1.529) had been formed.

Treatment of Phenylethyl Iodide with Iodine Monochloride.—To 9 g. (1 mol) of phenylethyl iodide in a small flask was added dropwise 6.2 g. (1 mol) of iodine monochloride. The reaction was very vigorous. Free iodine separated. The mixture was treated with 50 cc. of a cold 50% potassium iodide solution. The oil layer gave 4.1 g. of phenylethyl chloride, b. p. 82–84" (14 mm.), n_D^{20} 1.5295, a yield of 76%.

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(12) *Cf.* Whitmore and Lux, THIS JOURNAL, 54, 3451 (1932).

(13) Marvel, Gauerke and Hill, ibid., 47, 3009 (1925).

Summary

1. The action of iodine monochloride with several organic mercury compounds has been studied.

2. The products obtained are organic iodides except when a secondary reaction with the iodine chloride converts the organic iodide to a chloride.

3. The yields of organic iodides obtained are sufficiently high to justify the use of iodine monochloride in place of iodine in converting organic mercury compounds to organic iodides.

STATE COLLEGE, PENNSYLVANIA

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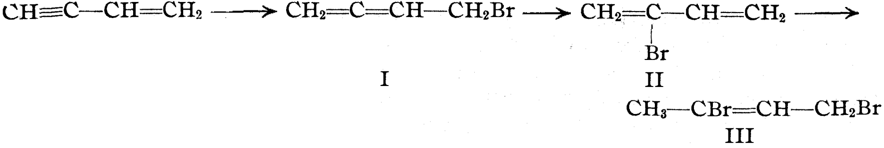
Acetylene Polymers and their Derivatives. IV. The Addition of Hydrogen Bromide to Vinylacetylene, Bromoprene and Dibromobutene

BY WALLACE H. CAROTHERS, ARNOLD M. COLLINS AND JAMES E. KIRBY

Observations on the combination of vinylacetylene with hydrogen chloride[1] have been extended to the analogous case of hydrogen bromide.

The two reactants are closely similar in their behavior, but hydrogen bromide appears to act somewhat more slowly than hydrogen chloride. Concentrated aqueous hydrobromic acid containing cuprous bromide, when shaken with vinylacetylene at the ordinary temperature, yields the two products, bromo-2-butadiene-1,3 (bromoprene, II) and dibromo-2,4-butene-2 (III). It seems likely, in view of the results already described for the hydrogen chloride reaction[1b] that the primary product of reaction between hydrogen bromide and vinylacetylene is bromo-4-butadiene-1,2 (I), which then rearranges to yield bromoprene, but no decisive direct evidence for the formation of this primary product is yet available. Its presence among the reaction products has not been established—even when no cuprous bromide (catalyst) was used. The structure of the dihydrobromide has not yet been directly established either, but formula III, in view of the results with hydrogen chloride, is not open to serious doubt.



$$CH\equiv C-CH=CH_2 \xrightarrow{HBr} \underset{\text{I}}{CH_2=C=CH-CH_2Br} \longrightarrow \underset{\text{II}}{CH_2=\underset{Br}{\underset{|}{C}}-CH=CH_2} \xrightarrow{HBr} \underset{\text{III}}{CH_3-CBr=CH-CH_2Br}$$

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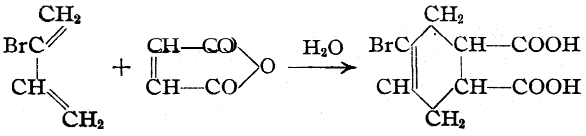
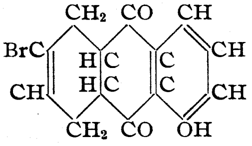
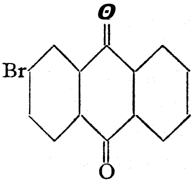
[1] (a) *Carothers, Williams, Collins and* Kirby, THIS JOURNAL, 63, 4203 (1931); (b) Carothers, *Berchet and* Collins. *ibid.*, **54**, 4066 (1932).

The third step in this series of reactions has a relatively high velocity, and appreciable amounts of the dihydrobromide (III) are present in the reaction mixture even at an early stage when the major part of the vinylacetylene applied remains unchanged. In this respect also the behavior of hydrogen bromide appreciably differs from that of hydrogen chloride.

Bromoprene is an oil having a faint greenish-yellow color and an odor rather closely resembling that of butyl bromide. It boils at 42 to 43° at 165 mm. The proof of its structure follows the course already indicated for chloroprene. It reacts with maleic anhydride to yield, after hydrolysis, a product whose composition agrees with that required for bromo-6-cyclohexene-5-dicarboxylic-2,3acid (IV). Bromoprene furthermore reacts readily with naphthoquinone. The primary product is a crystalline solid, which probably has the formula bromo-2-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (V). It is rapidly oxidized by air in alkaline solution to *β*-bromoanthraquinone (VI).


IV


V


VI

Experimental Part

Preparation of **Bromoprene.**—Fifty grams of cold vinylacetylene was placed in a pressure bottle containing 225 cc. of a thoroughly chilled solution prepared by dissolving 75 g. of moist, freshly prepared cuprous bromide in 200 g. of concentrated hydrobromic acid (sp. gr. 1.55). The bottle was allowed to warm up to room temperature and was then mechanically shaken for seven hours. After standing overnight and shaking for another two hours the unused vinylacetylene was allowed to evaporate. The residual oil was separated, washed with water, dried over calcium chloride and distilled from hydroquinone under reduced pressure. Dry, oxygen-free nitrogen was led through the capillary tube during the distillation. The yield of bromoprene boiling at 42–43° at 165 mm. was 30 g. (24%); d_4^{20}, 1.397; n_D^{20} 1.4988; M_R calcd., 27.50; M_R found, 27.94.

Anal. Calcd. for C_4H_5Br: C, 36.11; H, 3.78; Br, 60.15. Found: C, 36.32. 36.47; H, 4.13, 4.21; Br, 60.91, 61.43.

Higher yields were obtained by the use of more concentrated hydrobromic acid. For example, by using 2 moles of hydrobromic acid (sp. gr. 1.66) for each mole of vinylacetylene a yield of 44.8% of bromoprene was obtained.

Dibromo-2,4-butene-2.—After the distillation of the bromoprene a considerable amount of higher-boiling residue remained. From this residue there was obtained 12 g.

(6%) of a strongly lachrymatory, light yellow oil corresponding in analysis to a dibromobutene. It had the following physical constants: b. p. (760 mm.) 168 to 169° with loss of HBr; b. p. (23 mm.) 73°; d_4^{20} 1.8768; n_D^{20} 1.5485; M_R calcd., 35.74; M_R found, 36.25.

Anal. Calcd for $C_4H_6Br_2$: C, 22.43; H, 2.80; Br, 74.77. Found: C, 22.98, 23.06; H, 3.05. 2.95; Br, 74.94, 75.34.

Reaction of Bromoprene with Maleic Anhydride. Preparation of Bromo-6-cyclohexene-5-dicarboxylic-2,3 Acid.—To 5 g. (0.037 mole) of bromoprene was added 3 g (0.030 mole) of maleic anhydride. After the mixture had stood at room temperature for about one hour a spontaneous reaction set in and after three or four hours the mass solidified. The reaction product was then dissolved in benzene and shaken for twenty minutes with an excess of 10% sodium hydroxide. The aqueous layer was separated and acidified. The crude acid which separated was purified by recrystallization from water. It separated from water in the form of a mixture of thick plates and blunt needles melting sharply at 186.5 to 187°.

Anal. Calcd. for $C_8H_9O_4Br$: C, 38.57; H, 3.64; neutral equivalent, 124.5. Found: C, 38.37, 38.65; H, 3.75, 3.65; neutral equivalent, 125.4.

Action of α-Naphthoquinone on Bromoprene. Conversion to β-Bromoanthraquinone.—To a benzene solution of 15.4 g. (0.12 mole) of bromoprene was added 10 g (0.06 mole) of α-naphthoquinone. After standing at room temperature for two days the solution was gently refluxed for one hour. The benzene was then distilled off under reduced pressure. The residual sticky, dark red solid was pressed on a porous tile and then extracted with warm alcohol. The alcohol was decanted from an insoluble tar and, on cooling, 4.9 g. (49%) of unchanged naphthoquinone crystallized out. When the alcohol mother liquor was diluted with water, 2.6 g. of a nearly black solid separated. After recrystallization from alcohol it was obtained in the form of small, soft, nearly white crystals. When slowly heated on a copper block it began to turn blue at about 115° and slowly deepened in color as the temperature was raised At 138° it melted sharply; as the temperature was raised further it volatilized completely.

The analyses corresponded with the values calculated for bromo-2-tetrahydro-1,4,4a,8a-anthraquinone-9,10.

Anal. Calcd. for $C_{14}H_{11}O_2Br$: C, 57.74; H, 3.99 Found: C, 57.66, 57.65; H, 3.89, 4.04.

About 0.1 g. of the substance was dissolved in alcohol and a few drops of 10% sodium hydroxide solution added. The solution was dark red in color. As air was bubbled through the solution, the red color gave way to green, which in turn disappeared leaving a yellow solid. After recrystallization from amyl alcohol the oxidation product melted at 205–207°. β-Bromoanthraquinone melts at 207°[2]

Summary

Vinylacetylene reacts with aqueous hydrobromic acid to form bromo-2-butadiene-1,3 (bromoprene) and dibromo-2,4-butene-2. Bromoprene reacts with maleic anhydride yielding bromo-6-cyclohexene-5-dicarboxylic-2,3 acid, and with naphthoquinone yielding a bromotetrahydroanthraquinone which is readily oxidized to β-bromoanthraquinone.

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[2] Heller, *Ber.*, **45**, 672 (1912)

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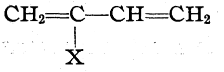
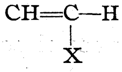
Acetylene Polymers and their Derivatives. V. The Polymerization of Bromoprene (Third Paper on New Synthetic Rubbers)

BY WALLACE H. CAROTHERS, JAMES E. KIRBY AND ARNOLD M. COLLINS

Chloroprene (I, X = Cl) polymerizes spontaneously to yield a rubber-like product,[1] and the speed of this transformation is roughly 700 times greater than the analogous transformation of isoprene. The present paper deals with the behavior of bromoprene[2] (I, X = Br), and the results may be summarized in the statement that it shows no significant qualitative differences from chloroprene, although its speed of polymerization under most conditions appears to be somewhat greater.


$CH_2{=}C(X){-}CH{=}CH_2$

I


$CH{=}C(X){-}H$

II

In connection with the behavior of these materials the following analogies are of interest. Vinyl chloride and vinyl bromide (II, X = Cl and Br) polymerize spontaneously yielding products of very high molecular weight,[3] but this behavior is not shown by propylene, which polymerizes only in the presence of special catalysts or under drastic conditions and then yields products having only moderately high molecular weights. The haloprenes (I) bear the same structural relationship to isoprene that the vinyl halides bear to ptopylene. Thus the very powerful activating effect of a single halogen atom on ethylene is also manifested in butadiene (when the halogen atom is on the β-carbon). The rate of polymerization is of great importance in studying the behavior of dienes since a high rate not only makes it possible to obtain experimental results in a reasonable length of time, but it permits one to extend the observations over a wide range of conditions. It becomes possible then to recognize the different types of reactions involved in the spontaneous polymerization and to obtain data on the way in which these different types of reactions are affected by changes in the conditions. Data of this type on chloroprene have already been presented, and it will be useful to review them briefly (with some extensions) and to make comparisons with those now available for bromoprene and for other dienes.

The polymerization of chloroprene leads to the four well defined and qualitatively distinct types of polymers shown in the chart.

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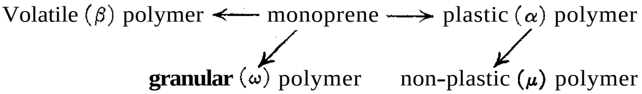
(1) Carothers, Williams, Collins and Kirby, THIS JOURNAL, 53, 4203 (1931).

(2) Carothers, Collins and Kirby, *ibid*, 55, 786 (1933).

(3) Staudinger, Brunner, and Feisst, *Helv. Chim Acta*, 13, 805 (1930).



The influence of various conditions on each of these reactions is indicated in Table I.

TABLE I

INFLUENCE OF CONDITIONS ON THE POLYMERIZATION OF CHLOROPRENE

Condition	Monoprene to β-polymer	Monoprene to or-polyprene	a-Polyprene to μ-polyprene	Monoprene to ω-polyprene
Temperature	+++	+	+	Autocatalytic, initiated by strong ultraviolet light and by metal surfaces
Pressure	+	++	+?	
Light	0	++	0?	
Oxygen	0	+++	++?	
Antioxidants	0	– – –	±[a]	

[a] Certain substances commonly classified as antioxidants (*e.* g., phenyl-β-naphthylamine) act as inhibitors; others (*e.* g., benzidine) act as accelerators: + accelerates, 0 no effect. – inhibits.

Of these different types of polymers the most important are the a- and the μ-polyprenes since the former corresponds to unvulcanized rubber and the latter corresponds to vulcanized rubber.

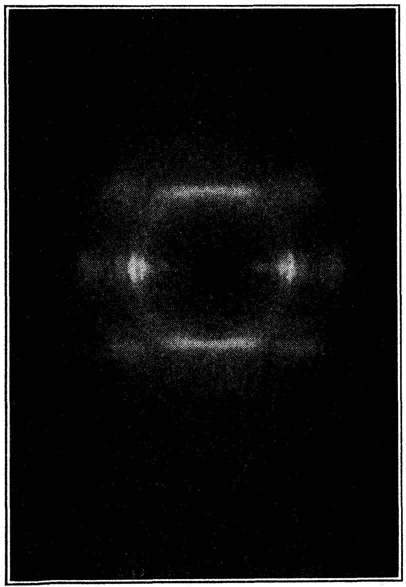


Fig. 1.—x-Ray diffraction pattern of μ-polybromoprene (from latex) stretched 500%.

The p-polyprene is the final product of the spontaneous polymerization of chloroprene; the a-polyprene is an intermediate step in the formation of the p-product. Isolation of the α-polymer free of p-polymer is possible only when the reaction is conducted under certain conditions: the temperature must not be too high, since elevated temperature accelerates the transformation of a-polymer to μ-polymer more than it accelerates the formation of a-polymer from monomer; the reaction must not be too slow, since most inhibiting influences have a greater decelerating effect on the formation of the α- than on the p-product; moreover, very slow reaction frequently leads to the formation of the w-polymer. Light and pressure both appear to have a greater accelerating effect on the formation of the a-polyprene than on the transformation of this into the p-polyprene.

The β-polymer, a terpene-like material, is an undesirable by-product in the rubber synthesis. In the chloroprene polymerization the production of β-polymer becomes appreciable only at temperatures higher than are necessary to bring about a rapid formation of a-polyprene. Butadiene, isoprene and dimethylbutadiene polymerize very slowly; to get the transformation to proceed at a reasonable rate, elevated temperatures are generally used, and this results in the formation of relatively large amounts of β-polymer.

The ω-polychloroprene is also a useless product; it is made up of discrete rubber-like particles (irregular globules) which are non-plastic and not even swelled by rubber solvents. The formation of this polymer is autocatalytic. When a speck of the ω-polymer appears (or is introduced) in a specimen of incompletely polymerized chloroprene, the entire specimen is soon more or less completely converted into the w-polymer. The formation of nuclei of the w-polyprene is favored by strong ultraviolet light and by metal surfaces (e. *g.*, sodium, potassium, mercury, iron, copper and aluminum). The opportunities for the formation of such nuclei are also increased by a long reaction time under any particular set of conditions. Similar polymers, frequently described as cauliflower-like masses, have been obtained from isoprene, butadiene and dimethylbutadiene, and one suspects that they may be the forms in which the polymers of these dienes are most frequently obtained. The very slow rate of the polymerization of these dienes would be especially favorable to the formation of o-polymer.

The term rubber-like is vaguely used to cover a multitude of the most diverse properties, and the literature of synthetic rubber is exceedingly obscure. Most of the agencies that are available to hasten the very slow polymerization of isoprene and butadiene are such as have been found in the case of chloroprene to affect more strongly the conversion of the a- into the μ-polymer than the formation of the a-polymer. One may expect therefore that the isolation of a true α-polyprene[4] from the isoprene and butadiene products will present especial difficulties. So far as we are aware no clear disclosure has ever been made of an a-polyprene from isoprene or from butadiene. However, when isoprene is subjected to a pressure of 12,000 atmospheres until 30% of the isoprene has polymerized, the polymer is at least 90% soluble in ether.5 If the reaction is allowed to proceed further until 80% of the isoprene has polymerized, the product is completely insoluble.[5,6] Thus the formation of a completely vulcanized

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(4) With the aid of swelling agents, softeners, and lubricants it is possible to confer a certain amount of plasticity on μ-polychloroprene. It is also possible to obtain from chloroprene plastic polymers that, on being heated, lose their plastic properties very incompletely or not at all. The material that we refer to as a-polychloroprene is an inherently plastic, *polymerizable* polymer; its plastic properties are completely lost and its elastic properties become fully developed when it stands or is heated

(5) Conant and Tongberg, Tars JOURNAL, 63, 1667 (1930).

(6) According to observations made by Dr. H. W. Starkweather in this Laboratory, isoprene polymers prepared in this manner are also completely non-plastic.

rubber-like product without the aid of sulfur is by no means peculiar to chloroprene. In fact the differences between the behavior of chloroprene and the behavior of other dienes appear to be differences of degree rather than differences of kind.

The Spontaneous Polymerization of **Bromoprene.**—A sample of bromoprene when allowed to stand at the ordinary laboratory conditions in a stoppered flask containing a small amount of air becomes noticeably more viscous after twelve to fifteen hours. As the reaction proceeds, the viscosity increases; after about five days the sample sets to a stiff, elastic jelly containing a considerable amount of unchanged bromoprene. Usually after eight to ten days all of the bromoprene has reacted, but the time required varies considerably in different experiments. The product has a density of about 1.74, and this is 24% greater than the density of the bromoprene. (The increase in density in the formation of μ-polychloroprene is about 28%.)

This product, p-polybromoprene, corresponds in its properties with the p-polychloroprene already described. It is tough, resilient, and elastic but harder than the analogous product from chloroprene. On standing it gradually undergoes further change: it becomes still harder and less extensible and the resemblance to soft vulcanized rubber pretty largely disappears although it still remains very tough and retains considerable elasticity and resiliency. These changes in the nature of the product are due, at least in part, to a progressive action of air and they can be retarded by the application of antioxidants to the surface of the sample. μ-Polybromoprene is similar to p-polychloroprene in its behavior toward solvents. It is greatly swelled by chloroform, carbon tetrachloride and aromatic hydrocarbons but remains practically unchanged after prolonged immersion in alcohol, ether, or aliphatic hydrocarbons such as gasoline.

α-Polybromoprene.—The preparation of an a-polybromoprene (plastic polymer) presents no difficulties. A sample of bromoprene was exposed to light from a Cooper–Hewitt lamp at 25°. After twenty-four hours 50% of the material had been converted into polymer. (This rate is about 40% greater than that usually obtained with chloroprene under the same conditions.) The product was an exceedingly viscous, yellow sirup. When it was mixed with a large volume of alcohol the a-polybromoprene was precipitated as a soft, plastic mass. This product showed no tendency to resist permanent deformation and sheeted out very readily on cold rolls. Two per cent. of phenyl-β-naphthylamine was worked into the plastic mass to prevent spontaneous conversion into an elastic polymer,' The sample was compounded with about 5% of its weight of zinc oxide and heated in a mold at 120 to 125° for twenty minutes. The product was non-plastic, strong, resilient and extensible (500 to 700%). However,

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(7) Ref. 1, p. 4219.

compared with a similar product from chloroprene it was somewhat lacking in snap, and its permanent set was rather high. It also showed a greater tendency to "freeze." After about two hours at ordinary temperatures it became very stiff, but the original pliability was restored when it was heated to 80° for a few minutes.

The Polymerization of Bromoprene in Aqueous Emulsion.--Like chloroprene, bromoprene is readily dispersed in water and the resulting smooth emulsion polymerizes with great rapidity to form a stable latex. The preparation and polymerization of such an emulsion is illustrated in the following example.

Twenty-five cubic centimeters of 2% aqueous sodium oleate in a wide-mouthed bottle was surrounded by a bath of ice and water. Two drops of triethanolamine was added to the solution, and then, with vigorous stirring, 25 g. of bromoprene. A smooth, milk-like emulsion resulted. After the mixture had stood in the ice-bath for five hours an aliquot portion was removed and poured into a large volume of alcohol. The weight of the precipitate thus obtained indicated that 78% of the bromoprene had polymerized. Under the same conditions chloroprene is only about 20–30% polymerized. The bromoprene emulsion described above was transferred to a refrigerator. After seventeen hours, more than 95% of the bromoprene had polymerized. Five cubic centimeters of 3% ammonium hydroxide was added to stabilize the emulsion and a small amount of an aqueous dispersion of phenyl-β-naphthylamine (2% on the rubber content) added to function as an antioxidant. The resulting latex was very stable.

As in the case of polychloroprene, the dispersed particles in the synthetic latex derived from bromoprene correspond more closely to the μ- than to the α-polymer. Nevertheless, when the latex is coagulated by the addition of acids, the particles coalesce and cohere very firmly. The coagulum is at first soft and plastic, but it quickly becomes tough, elastic and non-plastic. Homogeneous, coherent films are obtained by allowing the water to evaporate from a thin layer of the fluid latex on a plate of porous porcelain. The films are readily stripped from the plate and the removal of the water can be completed by drying them for a few hours in an oven at 80°. Such films are exceedingly tough and more resistant to tearing than analogous films prepared from chloroprene latices. A typical specimen had a breaking strength of 160 kg./sq. cm. and an elongation at break of 740%. (The elongation of similar polychloroprene films is usually about 800%.) The films exhibited the high permanent set and the tendency to freeze or stiffen already referred to in connection with the vulcanized α-polybromoprene. Like the latter, they were non-plastic and did not dissolve but merely swelled in chloroform and benzene.

β-Polybromoprene.—The conversion of bromoprene into a volatile liquid polymer (β-polybromoprene) occurs under conditions similar to those already described for chloroprene.[8] A sample of bromoprene containing about 5% of thiodiphenylamine, a substance which powerfully inhibits the conversion of the haloprenes to rubber-like' polymers, was

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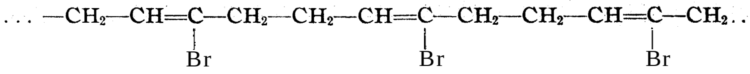
(8) Ref. 1, p. 4211

heated in a sealed tube at 80° for five days. When the resulting black oil was poured into alcohol a small amount of a black tar separated. From the alcohol there was obtained by distillation a small amount (about 15%) of a yellow oil boiling at 104 to 110° at 11 mm. It had a fragrant, terpene-like odor very similar to that of β-polychloroprene and was a mild lachrymator. It showed no tendency to polymerize further.

ω-Polybromoprene.—The formation of ω-polybromoprene, like the formation of ω-polychloroprene, occurs under conditions which result in very slow polymerization. For example, samples of bromoprene containing 0.2% of phenyl-β-naphthylamine or 0.5% of tetramethylthiuram disulfide and 0.3% of sulfur slowly became more viscous and, after two to six weeks, a white deposit having a crystalline appearance began to form. After formation of this substance had started, conversion of the whole mass was complete in a few days. The product turned dark brown in color on standing in air. ω-Polybromoprene is soft, opaque and noncoherent, while ω-polychloroprene is a mass of glistening, hard, rubbery granules. Like ω-polychloroprene, it is not swelled by benzene.

The Structure of Polybromoprene.—Evidence has already been presented for concluding that α-polychloroprene is precisely analogous to natural rubber in its chemical structure. The analogies between polychloroprene and polybromoprene are sufficiently close to justify the assumption of a similar structure (III) for the latter compound. The x-ray evidence is especially interesting. The fact that μ-polychloroprene when stretched furnishes a fiber diffraction pattern has already been disclosed.[1] Polybromoprene shows a similar behavior, but it furnishes an even sharper pattern (Fig. 1).[9] So far as we are aware, it has not been possible to obtain fiber diagrams from any other synthetic rubbers, and this fact perhaps justifies the conclusion that polychloroprene and polybromoprene are more regular in their molecular structure than any other known synthetic rubbers.

(III) 

$$\ldots -CH_2-CH=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2-CH_2-CH=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2-CH_2-CH=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2 \ldots$$

Summary

The polymerization of bromoprene is closely analogous to that of chloroprene, but somewhat more rapid. Spontaneous polymerization yields as the final product μ-polybromoprene, which resembles vulcanized rubber but is more dense than rubber or μ-polychloroprene. A plastic (α) polybromoprene is readily isolated from partially polymerized bromoprene, and it is converted to the μ-product by the action of heat. At elevated temperatures in the presence of inhibitors a volatile liquid (β) polymer is

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(9) The x-ray data will be discussed in more detail in a future paper by Dr. A. W. Kenney

formed. w-Polybromoprene, a granular, insoluble, rubber-like mass, is produced under conditions that lead to very slow polymerization.

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Studies in the Chlorophyll Series. IX. Transformations Establishing the Nature of the Nucleus

BY J. B. CONANT AND C. F. BAILEY

In previous papers of this series, the view has been put forward that the fundamental nucleus of chlorophyll *a* and the related phaeophorbides and chlorins is a reduced porphyrin ring. Such a formulation was largely based on spectroscopic data obtained at low temperatures.[1] We have now been able to obtain very convincing evidence of the correctness of this hypothesis by showing that a typical chlorin (chlorin f) can be oxidized to a porphyrin.

The dehydrogenation of chlorin f can be brought about either by the action of potassium ferricyanide on an alkaline solution at room temperature (the reaction is very rapid) or by the action of air on a hot alkaline solution of the complex metal salts of the chlorin. The latter method of converting chlorins to porphyrins has been used by Fischer in reoxidizing the "synthetic chlorins" prepared by reduction of the porphyrins.[2] It is clear that chlorin f is entirely analogous and is a reduced porphyrin. Since in chlorin f the side chain attached to the bridge has been removed, the failure of chlorin e to be so readily oxidized to a porphyrin can be attributed to the presence of the other functional groups. The number of hydrogen atoms present in chlorin f in excess of a porphyrin can be taken quite definitely as two, since one or three is excluded by valency considerations and four seems excluded by the analyses of chlorin f and its ester. The found and calculated percentages of hydrogen in the dimethyl ester and the free chlorin are as follows (paper IV): ester, found 7.05, 6.9, calcd. dihydro 7.04, tetrahydro 7.37; free chlorin, found 6.3, 6.6, calcd. dihydro 6.67, tetrahydro 7.02.

Chlorin f is a dibasic acid containing no group on a bridge atom, since it is readily converted to rhodoporphyrin by reduction with hydrogen iodide and reoxidation. However, the porphyrin which is formed from it by direct dehydrogenation is not rhodoporphyrin but an isomeric porphyrin which we shall designate as isorhodoporphyrin. It is identical with the

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(1) Conant and Kamerling, THIS JOURNAL, 63, 3522 (1931). Since the publication of this paper, the measurements of Kistiakowsky and Arnold there referred to have been published [*ibid.*, 64, 1713 (1933)]. A comparison of the ultraviolet absorption spectra at low temperature of benzene and cyclohexadiene (Fig. 2, K. and A.) with the absorption spectra of *aetioporphyrin* and chlorin e (Figs. 1 and 3, C. and K.) also at low temperature shows in a very striking way the resemblance of the porphyrin–chlorin relationship to that of benzene *vs.* cyclohexadiene.

(2) Fischer and Helberger, Ann., 471, 285 (1929).

porphyrin described in paper IV which was obtained as by-product in the pyrolysis of phaeopurpurin 7 and whose isomerism with rhodoporphyrin we commented on at that time. Subsequently the same substance was isolated by Fischer[3] by boiling dimethylphaeopurpurin 7 with pyridine; one would be inclined to assume that it was identical with verdoporphyrin except that Fischer explicitly states that it is not and calls it pseudoverdoporphyrin. We have never been able to prepare verdoporphyrin in this Laboratory and therefore could not make a direct comparison.

Isorhodoporphyrin can be converted into rhodoporphyrin by reduction. with hydrogen iodide and reoxidation of the resulting leuco compound with air. It can also be transformed into rhodoporphyrin by the action of strong alkali at 185–190°. The cause of the isomerism between isorhodoporphyrin and rhodoporphyrin is a matter of great interest and is clearly of the utmost importance to the chemistry of chlorophyll *a* since the fundamental nucleus of this compound is a dihydroisorhodoporphyrin. It seems probable that the isomerism may be due to a difference in the position of the two hydrogen atoms attached to the nitrogen atoms of the pyrrole nuclei in the porphyrin. If such isomers are capable of independent existence, a number are possible for an unsymmetrical porphyrin like rhodoporphyrin. However, one would expect that such isomers would yield the same complex metallic salt with a given metal—zinc for example. Isorhodoporphyrin and rhodoporphyrin, however, both form individual metallic complex salts with zinc from which each is regenerated without any evidence of interconversion. If the two zinc salts of these porphyrins are to be formulated as complex salts with all four nitrogen atoms involved, they are electronic isomers, which seems unlikely. Similar unexplained porphyrin isomers have appeared elsewhere in the degradations of chlorophyll *a* and in each case reduction with hydrogen iodide and reoxidation causes a conversion to the porphyrin of known structure. Pyrochlorin *e* porphyrin (pyrochloroporphyrin) for example[4] is isomeric with phylloporphyrin and by the decarboxylation of isorhodoporphyrin we have obtained small quantities of what appears to be an isopyrroporphyrin. We hope that experiments which are in progress in this Laboratory on the alkylation of porphyrins may throw light on this peculiar isomerism.

The establishment of the fact that chlorin f is a dihydroporphyrin can be used to settle the question of the state of oxidation of phaeophorbide a. If we let the entire porphyrin molecule be represented by the symbol P, then chlorin f is PH_2 and the unstable chlorin (or the isomeric phaeopurpurin) from which it is formed by loss of carbon monoxide and carbon dioxide must be $PH_2C_2O_3$. These compounds contain two hydrogen atoms less than the phaeophorbides or the tribasic acid, chlorin *e*, which is,

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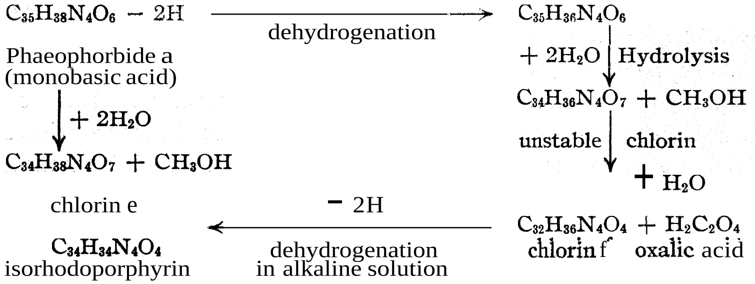
(3) Fischer, Ann , 490, 87 (1931).

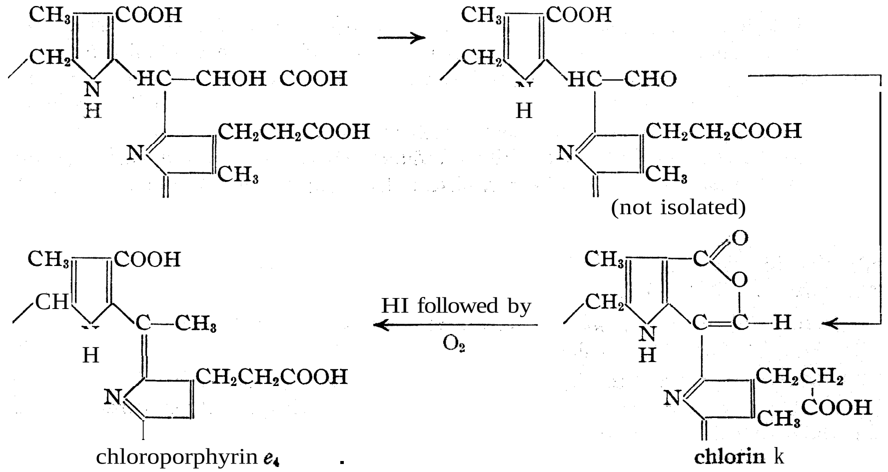
(4) Conant and Hyde, THIS JOURNAL, 51, 3674 (1929); 53, 367 (1931)

therefore, $PH_4C_2O_3$ = $C_{34}H_{38}N_4O_7$ which corresponds to our previous formula (see I below). Free phaeophorbide corresponds in composition to a monomethyl chlorin *e minus* water, and is, therefore, $C_{35}H_{38}N_4O_6$.[4a] Its transformation to isorhodoporphyrin is given by the following reactions in each of which there can be no doubt of the stoichiometric relations of factors and products.



The nucleus of the phaeophorbides and chlorophyll a is thus a dihydroporphyrin ring. Chlorin *e* is a dihydroisorhodoporphyrin with the lactic acid residue on one of the bridge carbon atoms; in our opinion it is still an open question as to the nature of the ring which is present in the phaeophorbides (and the chlorophyllides) and which opens on hydrolysis to yield chlorin *e*. We shall deal further with this problem in later papers.

The most satisfactory evidence for the presence of the lactic acid residue in chlorin *e* is its oxidation by molybdicyanide, yielding carbon dioxide.[5]



(4a) Since this paper was submitted for publication we have become convinced that the analyses of the purest samples of phaeophorbide *a* correspond to $C_{35}H_{36}N_4O_5$ as given by Willstäter. Stoll [Die *Naturwissenschaften*, 628 (1932)] and Fischer [*Ann.*, 499, 84 (1932)] have arrived at the same conclusion. The implications of this fact are discussed in two papers which are being submitted for publication

(5) Conant, Dietz, Bailey and Kamerling, *ibid.*, 63, 2392 (1931).

The resulting chlorin, chlorin k, is a monobasic acid yielding a mono ester whose analysis corresponds to the formula indicated below. On reduction with hydrogen iodide and reoxidation with air it is converted into a dibasic porphyrin which was prepared some time ago by Fischer and named by him chloroporphyrin e_4.

Its structure has been established by Fischer as a methylrhodoporphyrin. A similar transformation in the b series is the oxidation of rhodin k to rhodin n; it would be represented by the same series of reactions except that the group CO replaces CH_2 in the porphyrin (shown to the left in each formula). Rhodin *n* forms a monosemirarbazone, chlorin k forms no semicarbazone; this shows that in each case the aldehyde group formed by the oxidation of the hydroxy acid has been masked by lactone formation. The transformation of rhodin *n* to a porphyrin has not yet been studied.

Experimental Part

Isorhodoporphyrin from Chlorin *f*.—A solution of 150 mg. of chlorin f (0.28 millimole) in 75 cc. of 0.1 N potassium hydroxide was mixed with 30 cc. of 9.03 M potassium ferricyanide (0.9 millimole). After two minutes the solution was acidified and the organic material transferred to ether. A great deal of insoluble "scum" was formed which carried some porphyrin. The scum was therefore dissolved in pyridine and the mixture diluted with ether to recover more porphyrin. Acid fractionation of the ethereal solution showed that isorhodoporphyrin is the sole soluble product; it was removed with 6–9% hydrochloric acid and retransferred to ether in the usual manner. The yield of crystalline porphyrin was 25–35 milligrams. Experiments in which the amount of ferricyanide or the time of reaction was varied did not increase the yield. The use of less than three equivalents of reagent left some chlorin unattacked.

A solution of 100 mg. of chlorin f in 100 cc. of 10% sodium hydroxide was treated with about 300 mg. of a mixture of magnesium oxide and zinc oxide and boiled for three hours in a current of oxygen. The product worked up in the usual manner after decomposing the complex salts with strong acid yielded 11 mg. of crystalline isorhodoporphyrin; there was no other colored ether-soluble product. The acid number of the porphyrin is 6. Color in acid: violet, with a red fluorescence. Spectrum in ether: (1 mg in 1 cc. of pyridine and 29 cc. of ether, observed through a thickness of 50 mm.) I 645.1—640.8; II, 594.1---586.0—583.7---578.8—575.0; III, 558.6—539.5---536.9; IV, 519.8---517.1—502.9---498.2. E. A. 447.3. Order: III, IV, II, I. Spectrum in 9% hydrochloric acid: I, 664 5—654 4; II, 622.4---598.0; III, 585.8---575.5—540.9; IV, 528.5—520.4. E. A. 447.0. Order: 11,111, I, IV.

Anal. Calcd. for $C_{32}H_{34}O_4N_4$: C, 71.38; H, 6.32; N, 10 41. Found: C, 70 96, 71.17; H, 6.24, 6.51; N, 10.0, 9.8; OCH_3, 0.

Isorhodoporphyrin Dimethyl Ester.—This ester was prepared by the action of diazomethane on isorhodoporphyrin. The spectra in acid and ether were identical with those of the free porphyrin. Melting point (block) 264° (softens 261°); mixed melting point with ester from dimethylphaeopurpurin 7 by Fischer's procedure 260–261°; melting point of Fischer's porphyrin 260°; acid number, 9.

Anal. Calcd. for $C_{34}H_{38}O_4N_4$: C, 72.08; H, 6.71; N, 9.89; OCH_3, 10 95. Found. C, 72.08, 72.09; H, 6.92, 7.20; N, 9.70, 9.68; OCH_3, 10.34, 10.15.

The monomethyl ester of isorhodoporphyrin was described in paper IV, p. 370 (including analysis).

Transformations of **Isorhodoporphyrin.**—A solution of 25 mg. of isorhodoporphyrin in boiling anthracene was heated for three minutes. On fractionation there was obtained pyrroporphyrin (identified by acid number and by comparison of acid and ether spectra with a known sample), and a porphyrin extracted by 4 and 6% acid. This was neither pyrroporphyrin nor unchanged isorhodoporphyrin. It will be investigated later.

A solution of 10 mg. of isorhodoporphyrin in 10 cc. of acetic acid was reduced on a steam-bath for two and a half minutes with 2 cc. of hydrogen iodide (45%), and worked up in the usual way. About one-quarter of the material had been transformed into rhodoporphyrin There was also considerable unchanged isorhodoporphyrin, which on another reduction gave a further quantity of rhodoporphyrin.

A solution of 15 mg. of isorhodoporphyrin dimethyl ester in 1 cc. of pyridine was mixed with 50 mg. of mixed zinc and magnesium oxides and 5 cc. of 25% methyl alcoholic potash. The whole was heated in a bomb tube filled with nitrogen for seven hours at 185–190°. On treatment with acid to destroy the metallic complexes and acid fractionation in the usual way, rhodoporphyrin and pyrroporphyrin were obtained, representing about one-third of the material, the rest being unchanged isorhodoporphyrin The identification of rhodoporphyrin and pyrroporphyrin was by acid number and spectrum. Similar experiments at 120–140° for five hours gave only a trace of conversion.

Chloroporphyrin *e_4* from **Chlorin** k.—The yield of chlorin k from chlorin e was increased from that reported in paper IV to 37% when 2 g. of chlorin e was oxidized at once. A sample of chlorin k (150 mg.) was dissolved in 125 cc. of glacial acetic acid; 15 cc. of hydriodic acid (sp. gr. 1.45) was added and the mixture heated on the steam-bath for two and a half hours. The reaction mixture transferred to ether was washed with dilute ammonia until the acid had been removed and was allowed to stand for about two hours in contact with a slightly ammoniacal aqueous solution (to complete the reoxidation of the leuco compound). The material was then acid-fractionated in the usual manner. Chloroporphyrin *e_4* was extracted with 1% acid; from 500 mg. of chlorin k, 63 mg. of crystalline material was obtained. It was identified by conversion to the dimethyl ester with diazomethane and a comparison of this with a sample prepared by Fischer's procedure. Analysis, spectrum, acid number and melting point were identical (250–252°). A mixed melting point showed no depression.

In addition to chloroporphyrin *e_4*, there was obtained another porphyrin or mixture of porphyrins which was extracted with 4% acid. About 36 mg. of this material was obtained from 500 mg. of chlorin k. On treatment with diazomethane in ether solution it became alkali insoluble. The methoxyl determination indicated only about a group and a half. Color in acid: blue-green. Spectrum in ether of mixed porphyrins: (chloroporphyrin *e_4*) I, 635.5—631.4; II, 590.0–579.9—575.6; III, 557.4—545.0–541.1; IV, 523.4–518.8—502.9–500.0. E.A. 439.5. Order: III, IV, II, I. Spectrum in 7% hydrochloric acid: I, 626.4–621.6—615.1–605.9—600.5; II, 582.8–578.4—550.0–545.6. E.A.442.7. Order: II, I.

Rhodin n.—The oxidation of rhodin g to yield rhodin *n* was carried out in exactly the same manner as the oxidation of chlorin e.

An oxidizing solution was prepared by dissolving 1.66 g. of potassium molybdocyanide in 100 cc. of water and 10 cc. of glacial acetic acid, oxidizing with potassium permanganate, pouring into a mixture of 500 cc. of acetone and 67 cc. of pyridine, making up to 750 cc. with water, and filtering; 500 mg. of rhodin g was added, and after allowing five hours for the reaction, the mixture was poured into 6 liters of ether, washed, and fractionated. Extraction with 12–16% acids removed impure material, which was discarded, while rhodin *n* was extracted by 18 and 20% acid. The material was refractionated to remove small amounts of impurities: yield, 89 mg.; acid number, 17. Spectra reported in paper VIII, p. 4443.

Anal. Calcd. for $C_{33}H_{32}O_6N_4$: C, 70.21; H, 5.67; N, 9.93. Calcd. for $C_{33}H_{34}O_6N_4$:

C, 68.04; H, 5.84; N, 9.62. Found: C, 67.60. 68.44, 68.09; H, 5.50, 6.58, 6.09; N, 9.90, 9.80; OCH_3, 0.58, 1.0.

Rhodin *n* Monomethyl Ester.—This compound was prepared by the action of diazomethane on **rhodin** ***n*;** spectra the same as **rhodin *n*.** The melting point is indefinite; it sinters at 140–150°.

Anal. Calcd. for $C_{04}H_{34}O_5N_4$: C, 70.59; H, 5.88; N, 9.69; OCH_3, 5.36. Found: C, 69.04, 68.36, 68.85; H, 6.68, 6.11, 6.28; N, 8.77, 8.94; OCH_3, 5.20, 5.94.

Semicarbazone of **Rhodin *n* Monomethyl** Ester.—Sixty mg. of the ester and 250 mg. each of sodium carbonate and semicarbazide hydrochloride were mixed in 20 cc. of pyridine, and allowed to stand at room temperature for forty-five minutes. After two minutes the wine-red color changed to olive-green and the spectrum bands spread apart. The mixture was put into 2 liters of ether and washed well with cold water and cold 1% hydrochloric acid. The ether solution was greenish-yellow. The semicarbazone was rather insoluble and tended to form a scum; this was recovered and added to the main lot; yield, 25 mg.; acid number, 11; acid color, green. Spectrum in ether: I, 681.1—647.1; II, 613.0—601.6; III, 530.1---526.0—498.4. E.A.451.2. Order: I, III, II. Spectrum in 14% hydrochloric acid: I, 673.9---667.9—643.9---634.9; II, 543.2—529.2. E. A. 459.5 Order: I, II.

Anal. Calcd. for $C_{35}H_{37}O_5N_7$: C, 66.14; H. 5.82; N, 15.43; OCH_3, 4.88. Found: C, 65.13, 65.75; H, 6.33, 6.17; N, 13.79, 13 86; OCH_3, 5.00, 4.66.

Warming with 18% hydrochloric acid on the steam-bath for less than a minute was enough to regenerate **rhodin *n*.**

Attempt to Prepare a Semicarbazone of Chlorin k Ester.—One hundred mg. of chlorin k ester and 0.4 g. each of sodium carbonate and semicarbazide hydrochloride were added to 40 cc. of pyridine, and the mixture was refluxed for an hour. The mixture was poured into 2 liters of ether and washed well with cold 2% hydrochloric acid and cold water. There was no color or spectrum change. Analysis of the product proved that it was unchanged chlorin k.

Summary

1. A simple chlorin (chlorin f) obtained by degradation of chlorophyll *a* can be dehydrogenated to a porphyrin having the same carbon skeleton. This fact affords further evidence that the fundamental nucleus of the chlorophyll ***a*** molecule is a dihydroporphyrin ring.

2. Chlorin k, obtained from chlorin *e* by oxidative degradation, has been transformed into chloroporphyrin e_4. **Rhodin** g has been oxidized to **rhodin** *n* which contains **a** carbonyl group as do the other members of the b series.

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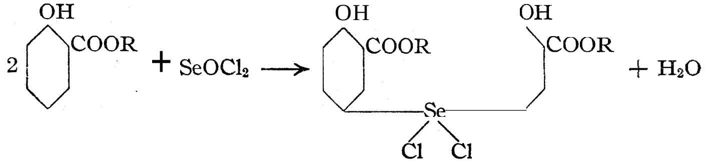
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

Organic Compounds of Selenium. III. The Action of Selenium Oxychloride upon Esters of Salicylic Acid[1]

BY R. E. NELSON, R. A. SCHROEDER AND W. R. BUNTING

The first paper[2] of this series discussed the action of selenium oxychloride upon ketones and the second paper[3] dealt with the action of selenium oxychloride upon ethers. In this investigation selenium oxychloride has been allowed to act upon methyl, ethyl, propyl, isopropyl, butyl, amyl and phenyl salicylates. The reaction takes place according to the equation



Their structure will be discussed in a later paper.

The resulting dialkyl 5,5′-seleno-disalicylate Se-dichlorides are converted to the dialkyl 5,5′-seleno-disalicylates by reduction with zinc

$$R_2SeCl_2 + Zn \longrightarrow R_2Se + ZnCl_2$$

The dialkyl 5,5′-seleno-disalicylate Se-dihydroxides have been prepared by treating the respective dichloro derivatives with sodium bicarbonate in aqueous solution

$$R_2SeCl_2 + 2HOH \longrightarrow R_2Se(OH)_2 + 2HCl$$

The dialkyl 5,5′-seleno-disalicylate Se-dibromides and the corresponding iodo derivatives were prepared by the addition of bromine or iodine to seleno-salicylate derivatives in chloroform.[4]

The dichlorides, diiodides and disalicylates were yellow, the dibromides orange-red and the dihydroxides were white.

Experimental

The selenium oxychloride for these experiments was obtained from the J. T. Baker Company and used without further purification. The methyl salicylate and phenyl salicylate (salol) were obtained from the Mallinckrodt Chemical Works. The other esters were prepared in this Laboratory by the usual methods of synthesis.

The products were identified by analysis for selenium and halogen. Analysis for selenium[5] was carried out by fusion with sodium peroxide in a Parr bomb. The fused

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[1] R. R. LaMotte prepared a number of these compounds in this Laboratory but the work was not published.

[2] Nelson and Jones, THIS JOURNAL, 52, 1588 (1930).

[3] Alquist and Nelson, *ibid.*, 53, 4033 (1931).

[4] Kunckell prepared the iodo derivative by treating the dichloro derivative of a similar compound with potassium iodide in alcoholic solution [Kunckell, Ber., 28, 609 (1895)] The reaction was tried in this Laboratory but good results were not obtained. Some of the iodo derivative was formed but the major portion was reduced to the selenodisalicylate and free iodine was formed. This effect was greatly increased by the presence of small amounts of water

[5] Shaw and Reid, THIS JOURNAL, 49, 2330 (1927).

mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by addition of sulfur dioxide. Analysis for halogen was carried out in a similar way, except that nitric acid was used for acidifying and silver halide was precipitated by addition of silver nitrate. In some cases the Volhard volumetric method was used.

The melting points of these compounds are rather difficult to obtain, due to decomposition. The melting points were taken by raising the temperature rapidly until the compound melted. A second sample was then placed in the bath and heated slowly until it melted

The preparation of the methyl salicylate derivatives, which is typical of all the preparations, was as follows.

Dimethyl 5,5′-Seleno-disalicylate Se-dihalide.—Seventy-five grams of methyl salicylate was treated with an equivalent amount of the selenium oxychloride, plus a 10% excess (45 g.). The two were shaken together and warmed only enough to start the reaction. The solution darkens and some hydrogen chloride is evolved. On cooling the mass solidifies. This is broken up, washed several times with ether and recrystallized from benzene. It is soluble in alcohol, ether and glacial acetic acid and is slightly soluble in benzene. The solubility in benzene increases with the higher homologs.

TABLE I

YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF DIALKYL 5,5′-SELENO-DISALICYLATE AND DERIVATIVES

	Dialkyl	Acidic radical	M. p., °C.	Yields, %	Formula	Analytical data, %			
						Selenium		Halogen	
						Calcd.	Found	Calcd.	Found
1	Dimethyl	Dichloride	176	25	$C_{16}H_{14}Cl_2O_6Se$	17.5	17.8	15.7	15.6
2	Diethyl	Dichloride	165	20	$C_{18}H_{18}Cl_2O_6Se$	16.5	16.6	14.8	15.7
3	Dipropyl	Dichloride	130	20	$C_{20}H_{22}Cl_2O_6Se$	15.6	15.5	13.9	14.0
4	Diisopropyl	Dichloride	173	46	$C_{20}H_{22}Cl_2O_6Se$	15.6	15.8	13.9	13.9
5	Dibutyl	Dichloride	133	20	$C_{22}H_{26}Cl_2O_6Se$	14.8	14.9	13.2	13.1
6	Diamyl	Dichloride	138	25	$C_{24}H_{30}Cl_2O_6Se$	14.0	13.3	12.5	12.6
7	Diphenyl	Dichloride	185	47	$C_{26}H_{18}Cl_2O_6Se$	13.7	14.0	12.3	12.3
8	Dimethyl		158	60	$C_{16}H_{14}O_6Se$	20.8	20.6		
9	Diethyl		88	58	$C_{18}H_{18}O_6Se$	19.3	19.3		
10	Dipropyl	Yellow viscous unstable liquid		34	$C_{20}H_{22}O_6Se$	18.1	17.8		
11	Diisopropyl		81	70	$C_{20}H_{22}O_6Se$	18.1	18.4		
12	Dibutyl	Yellow viscous unstable liquid		31	$C_{22}H_{26}O_6Se$	17.0	17.4		
13	Diamyl	Yellow viscous unstable liquid			$C_{24}H_{30}O_6Se$	No analysis made			
14	Diphenyl		138		$C_{26}H_{18}O_6Se$	15.7	15.1		
15	Dimethyl	Dibromide	143	41	$C_{16}H_{14}Br_2O_6Se$	14.6	14.6	29.5	29.5
16	Diethyl	Dibromide	147	39	$C_{18}H_{18}Br_2O_6Se$	13.9	13.8	28.1	28.3
17	Dipropyl	Dibromide	110	23	$C_{20}H_{22}Br_2O_6Se$	13.3	13.1	26.8	26.5
18	Diisopropyl	Dibromide	159	94	$C_{20}H_{22}Br_2O_6Se$	13.3	13.0	26.8	27.1
19	Dibutyl	Dibromide	95	19	$C_{22}H_{26}Br_2O_6Se$	12.7	12.5	25.6	25.3
20	Diamyl	Dibromide	121		$C_{24}H_{30}Br_2O_6Se$	12.1	11.9	24.5	25.0
21	Diphenyl	Dibromide	160		$C_{26}H_{18}Br_2O_6Se$	11.9	12.1	24.0	24.8
22	Dimethyl	Diiodide	150	24	$C_{16}H_{14}I_2O_6Se$	12.5	12.6	40.0	39.9
23	Diethyl	Diiodide	140	21	$C_{18}H_{18}I_2O_6Se$	11.9	11.6	38.3	38.4
24	Dipropyl	Diiodide	78	17	$C_{20}H_{22}I_2O_6Se$	11.5	11.6	36.7	36.3
25	Diisopropyl	Diiodide	96	95	$C_{20}H_{22}I_2O_6Se$	11.5	11.9		
26	Dibutyl	Diiodide	65	15	$C_{22}H_{26}I_2O_6Se$	11.0	11.3	35.3	35.0
27	Diamyl	Diiodide	Dark brown viscous liquid		$C_{24}H_{30}I_2O_6Se$				
28	Diphenyl	Diiodide	120		$C_{26}H_{18}I_2O_6Se$	10.4	11.1		
29	Dimethyl	Dihydroxide	137	37	$C_{16}H_{16}O_8Se$	19.1	18.2		
30	Diethyl	Dihydroxide	107	39	$C_{18}H_{20}O_8Se$	17.9	17.0		
31	Dipropyl	Dihydroxide	63	33	$C_{20}H_{24}O_8Se$	16.8	15.5		
32	Diisopropyl	Dihydroxide	83	83	$C_{20}H_{24}O_8Se$	16.8	17.2		
33	Dibutyl	Dihydroxide	57	31	$C_{22}H_{28}O_8Se$	15.9	15.4		
34	Diamyl	Dihydroxide	97	80	$C_{24}H_{32}O_8Se$	15.0	15.5		
35	Diphenyl	Dihydroxide	122	75	$C_{26}H_{20}O_8Se$	14.7	15.2		

The disalicylate was prepared from the above by treating with 10% excess of zinc dust in a 0.1 *N* chloroform solution of the derivative. This was refluxed for ten minutes after the solution became clear. The solution was filtered and the chloroform allowed to evaporate. The product was washed with alcohol. It is soluble in chloroform, ether and alcohol and is rather unstable

The bromides and iodides were prepared by adding 10% excess of halogen in chloroform solution to a chloroform solution of the corresponding disalicylate derivative. The chloroform was allowed to evaporate. The bromide was recrystallized from alcohol.

The iodide was washed with a solution of potassium iodide to remove the excess of iodine. It was then washed thoroughly with water and dried in a vacuum desiccator over calcium chloride The crystals were soluble in alcohol, ethe and chloroform.

The dihydroxide was prepared by treating the dichloride with warm distilled water containing 10% excess of sodium bicarbonate and allowed to stand for twenty-four hours at 40–50°. The original yellow compound changed to a practically white compound After filtering the product was recrystallized from hot alcohol. It was soluble in chloroform, ether, alcohol and very slightly soluble in water.

The corresponding derivatives of the other esters of salicylic acid were prepared in an analogous way and the yields, physical constants and analyses are summarized in the table.

Summary

1. The reaction between selenium oxychloride and certain esters of salicylic acid has been studied in which two molecules of the ester condensed with one molecule of selenium oxychloride.

2. The resulting selenium dichlorides can be hydrolyzed to produce selenium dihydroxides.

3. The reduction of the selenium dichlorides by zinc gives selenides.

4. The selenides readily add bromine or iodine, forming selenium dibromides and selenium diiodides.

LAFAYETTE, INDIANA

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

Local Anesthetics Derived from Dialkylaminopropanediols. II. Esters of Piperidinopropanediol[1]

BY E. W. SCOTT AND T. H. RIDER

In an earlier paper[2] one of us called attention to the fact that the phenyl carbamates of dialkylaminopropanediols were local anesthetics of merit. In a later publication[3] the same author pointed out that certain other phenyl carbamates were more active local anesthetics than the corresponding *p*-aminobenzoates at present on the market. During the pharmacological studies on the phenyl urethans of dialkylaminopropanediols[4] it was found that the corresponding aminobenzoates were inferior as local anesthetics (unpublished).

On the basis of further pharmacological and clinical study, the hydrochloride of piperidinopropanediol diphenylurethane (Diothane) has been selected as the best anesthetic among those previously discussed.

As a part of the further investigation of the relationship of physiological activity to the structure of various esters of piperidinopropanediol, we have made esters with the following acids: benzoic,[5] *p*-aminobenzoic,[6] p-tolylcarbamic and a-naphthyl carbamic. The first two esters named have been previously prepared and anesthetic activity attributed to them but no definite pharmacological data was given. The two carbamates are new, and in so far as the authors are aware, these acids have never been used in preparing local anesthetics.

Experimental

Piperidinopropanediol Di-a-naphthylurethan Hydrochloride.—A solution of 15.9 g. of piperidinopropanediol in 100 cc. of dry benzene was heated to the boiling point and a solution of 34 g. of a-naphthyl isocyanate in 50 cc. of dry benzene was slowly added. The mixture was heated for thirty minutes to complete the reaction, then cooled, filtered and a cold saturated solution of hydrogen chloride gas in dry benzene was added during stirring. The mixture was cooled overnight, the precipitate filtered off, washed with acetone, dissolved in a small volume of methyl alcohol and poured into acetone, precipitating 34 g. of piperidinopropanediol di-α-naphthylurethan hydrochloride; melting point 202–203°.

Anal. Calcd. for $C_{30}H_{31}O_4N_3 \cdot HCl$: Cl, 6.65. Found: Cl, 6.66, 6.72.

Piperidinopropanediol **Di-*p*-tolylurethan** Hydrochloride.—Following the above procedure, 40 g. of piperidinopropanediol and 77 g. of p-tolyl isocyanate were caused to

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(1) A preliminary report of this research was made before the Medicinal Section of the American Chemical Society. New Orleans, March, 1932.

(2) Rider, THIS JOURNAL, **52,** 211.5 (1930).

(3) Rider, *ibid.*, **52,** 2583 (1930).

(4) Rider, *J. Pharmacol.*, 39, 457 (1930)

(5) Pyman, J. *Chem. Soc.*, *93,* 1793 (1908).

(6) Einhorn, Piedler, Ladisch and Uhlfelder, *Ann.*, 371, 142 (1909).

react and the hydrochloride of the resulting ester precipitated and purified, yielding 70 g. of piperidinopropanediol di-p-tolylurethan hydrochloride; melting point 223–225°.

Anal. Calcd. for $C_{24}H_{31}O_4N_3$ HCI: Cl, 7.68. Found: Cl, 7.74, 7.72.

Pharmacological.-—All compounds were tested by Topical application to the cornea of the rabbit and by intradermal injection into the human forearm, following previously described techniques.[4] Toxicity determinations were made by subcutaneous injection into guinea pigs. The data on the different esters are summarized in Table I.

TABLE I

$ACOOCH_2CH(OCOA)\ CH_2NC_5H_{10}\cdot HCl$ COMPOUNDS

ACOOH	Concentration, molar	Duration of anesthesia (minutes) Rabbit cornea	Intradermal wheal	Tonicity. to guinea pigs LD_{50} Mg/Rg
Phenylcarbamic acid	9.00575	28	55	400
Tolylcarbamic acid	00575	50	42	250
Naphthylcarbamic acid	.00575	103	32	300
p-Aminobenzoic acid	.00575	Incomplete	23	150
Benzoic acid	.00575	Incomplete	12	> 600

The phenyl carbamate derivative was the most powerful anesthetic for injection and was only exceeded in its activity on the cornea by the two other urethans, both of which were decidedly irritating. Only the benzoate was less toxic than the phenyl urethan and the anesthetic activity of this compound was very low.

Summary

In a series of local anesthetics prepared from piperidinopropanediol, the di-phenyl carbamate is better than the di-a-naphthyl carbamate, the di-*p*-tolyl carbamate, the di-benzoate or the di-*p*-aminobenzoates.

CINCINNATI, OHIO

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

Hydroxy and Bromo Esters Derived from the Hydrogenation of Certain Omega-Acetyl Esters

BY ELMER J. LEASE AND S. M. MCELVAIN

Several years ago it was noted in this Laboratory that the hydrogenation of acetoacetic ester with Adams platinum oxide catalyst proceeded at a considerably slower rate than that of a simple ketone, such as acetone. The most apparent reason for this behavior was the close proximity of the carbethoxy group to the carbonyl group in the acetoacetic ester molecule.

Since a series of bromo esters of the type $CH_3CHBr(CH_2)_nCOOC_2H_5$ were needed for some other work, it seemed advisable to prepare them from the corresponding hydroxy esters derived from the hydrogenation of a series of ω-acetyl esters of the type $CH_3CO(CH_2)_nCOOC_2H_5$. This would make possible the determination of the effect of increasing the number of methylene groups between the carbethoxy and carbonyl group on the rate of hydrogenation of the latter group.

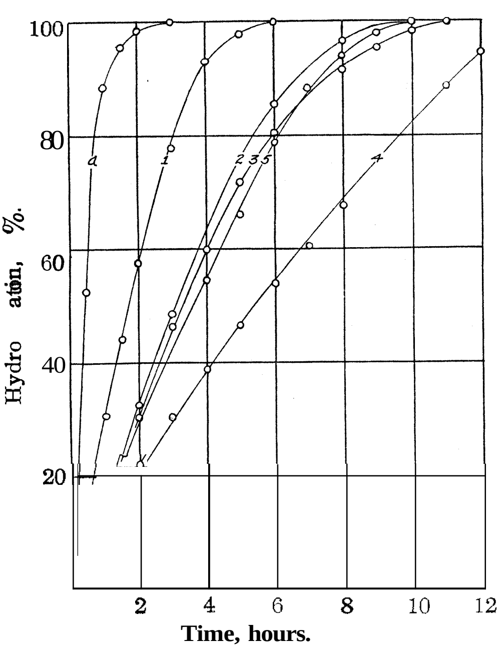

Fig. 1.—Rate of hydrogenation of ω-acetyl esters: Curve a, acetone; the number on each of the other curves is the value of n in the formula $CH_3CO(CH_2)_nCOOC_2H_5$

The results which were obtained with such a series of keto esters are illustrated in Fig. 1. A curve showing the rate of hydrogenation of acetone under similar conditions is included for comparison. In each instance **0.3** mole of the keto compound and **0.3** g. of Adams platinum oxide catalyst were used. These hydrogenations were made in alcohol solution, but the relative rates were practically the same when the hydrogenations were carried out without a solvent. It is seen from these curves that rate of hydrogenation of the keto esters does not approach that of acetone but continues, in general, to decrease as the value of n increases. The only explanation for the variation of the positions of Curves 4 and 5 from the regular order is that the keto ester in which n is 4 was prepared through a cyanide and may have contained a small amount of an impurity which lowered the rate of hydrogenation.

w-Acetyl Esters.—Acetoacetic ester was carefully distilled before use. Acetylsuccinic ester and acetylglutaric ester were prepared by the method described by Isbell, Wojcik and Adkins.[1]

Acetylpimelic ester was prepared by a similar procedure from acetoacetic ester and 6-bromovaleric ester.[2] This diester was not purified by distillation, but was used directly after it was freed from lower boiling associated products. These acetyl diesters were converted into the corresponding keto acids $CH_3CO(CH_2)_nCOOH$ by hydrolysis with dilute hydrochloric acid.[3] The acid.: so obtained were esterified in carbon tetrachloride solution.[4] The over-all yield of ethyl ω-acetylcaproate from ethyl 6-bromovalerate was 20% of the theoretical. The keto ester in which n is 4 was prepared by esterification of w-acetylvaleric acid.[5] The properties of these esters are summarized in the table. The esters in which n is 4 and 5 have not been described previously in the literature.

TABLE I

I. KETO ESTERS, $CH_3CO(CH_2)_nCOOC_2H_5$

n is	B. p., °C. (9 mm)	d^{25}_{25}	n^{25}_D	Analyses, % Calcd. C	H	Found C	H
1	64–65	...	....	...	...	...	...
2	82–83	...	....	...	...	...	...
3	94–95	...	....	...	...	...	...
4[a]	107–108	0.9795	1.4305	62.79	9.30	62.51	9.16
5	121–122	.9708	1.4375	64.52	9.68	64.26	9.62

II. HYDROXY ESTERS, $CH_3CHOH(CH_2)_nCOOC_2H_5$

n is	B. p., °C.	d^{25}_{25}	n^{25}_D	Calcd. C	H	Found C	H
1[b]	70–71 (9 mm.)	0.9496	1.4195	...	...	...	...
2[c]	85–86 (2 mm.)	.9532	1.4265	57.54	9.59	57.51	9.62
3	94–95 (2 mm.)	.9832	1.4315	60.00	10.00	59.62	9.98
4	103–104 (2 mm.)	.9714	1.4329	62.07	10.35	61.55	10.24
5	111–113 (2 mm.)	9621	1.4387	63 83	10 64	63.70	10.41

[a] This ester was used in a condensation by Blaise and Koehler, *Compt. rend.*, 148, 1401 (1909) but no description of its properties was given.

[b] Curtius and Müller, *Ber.*, 37, 1277 (1904), report this ester b. p. 170; *cf.* also Tischtschenko, *Chem. Centr.*, [11]1310 (1906).

[c] Both Neugebauer [*Ann.*, 227, 101 (1885)] and Thomas, Schuette and Cowley [THIS JOURNAL, 53, 3861 (1931)] report that this ester is converted by distillation into valerolactone. It was found, however, in the present work that no appreciable amount of this lactone is formed if the hydroxy ester is distilled rapidly from a Claisen flask with a short side arm.

Hydroxy Esters, $CH_3CHOH(CH_2)_nCOOC_2H_5$.—A solution of 0.3 mole of the keto ester in *35* cc. of absolute alcohol was shaken with hydrogen under 2–3 atmospheres of pressure in the presence of 0.3 g. of Adams platinum oxide catalyst until the theoretical amount of hydrogen was absorbed. After decantation from the catalyst, the alcoholic solution was distilled under diminished pressure from a Claisen flask without a fractionat-

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(1) Isbell, Wojcik and Adkins, THIS JOURNAL, 54, 3685 (1932).

(2) Merchant, Wickert and Marvel, *ibid.*, 49, 1828 11927).

(3) Fittig and Wolff, Ann., 216, 129 (1883).

(4) "Organic Syntheses," 1923, Vol. III, p. 51.

(5) Derick and Hess, THIS JOURNAL, 40, 551 (1918).

ing column. The yields of the hydroxy esters were **82–88%.** Their properties are summarized in Table I.

Bromo Esters, $CH_3CHBr(CH_2)_nCOOC_2H_5$.—To a solution of 0.3 mole of the hydroxy ester in 30 cc. of benzene was added slowly **0.1** mole of phosphorus tribromide. The flask containing the reactants was placed in an ice-bath and allowed to remain for half an hour. After this time the reaction mixture was gradually warmed to 60° and kept at this temperature for thirty minutes. It was then cooled, treated with **50** cc. of water, the layers separated and the aqueous layer extracted with an equal volume of benzene. The benzene extracts were combined, washed with water, dried over anhydrous sodium sulfate and distilled. The yields were **61–74%** of the theoretical. The properties of these bromo esters are listed in Table II.

TABLE II

BROMO ESTERS, $CH_3CHBr(CH_2)_nCOOC_2H_5$

				Analyses, %					
				Calcd.			Found		
n is	B. p., °C. (2 mm.)	d^{25}_{25}	n^{25}_{D}	C	H	Br	C	H	Br
1[a]	41–42	1.3103	1.4445	36.92	5.64	41.02	37.00	5.70	40.77
2	52–54	1.2330	1.4497	40.19	6.22	38.28	40.21	6.29	37.97
3	69–71	1.1943	1.4525	43.05	6.73	35.88	43.25	6.67	35.03
4	85–87	1.2028	1.4550	45.57	7.17	33.75	45.51	7.05	33.00
5	95–96	1.1660	1.4564	47.81	7.57	31.87	47.68	7.39	31.21

[a] Lespieau, *Chem. Centr.*, I, **24** (1905), notes this ester as boiling at **183** (*755* mm.).

Summary

The hydrogenation of a series of ω-acetyl esters, $CH_3CO(CH_2)_nCOOC_2H_5$, in which n varies from 1 to 5, has been described. The resulting hydroxy esters have been converted into the corresponding bromo esters.

The properties of the following compounds, not previously listed in the literature, are described: ethyl w-acetylvalerate, ethyl w-acetylcaproate, ethyl y-hydroxyvalerate, ethyl δ-hydroxycaproate, ethyl ε-hydroxyheptoate, ethyl ζ-hydroxycaprylate, ethyl y-bromovalerate, ethyl δ-bromocaproate, ethyl ε-bromoheptoate and ethyl ζ-bromocaprylate.

MADISON, WISCONSIN RECEIVED AUGUST 15, 1932
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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Color of Sulfuric Acid Solutions of Di- and Triphenylmethanes

BY LEIGH C. ANDERSON

A yellow color develops when sulfuric acid solutions of di- and triphenylmethanes are allowed to stand. The causes of the color of these solutions have been discussed by several investigators, most of whom suppose it to be due to the presence of impurities in the original materials. Baeyer and Villiger[1] assumed at first that the color was due to an acid salt of triphenylniethane but after Ullmann[2] had shown that triphenylmethane contained impurities which were removed by treatment with 75–80% sulfuric acid, they ascribed the production of the color of their solutions to the presence of anthracene. Baker,[3] Massol and Faucon,[4] and McVicker, Marsh and Stewart[5] have presented spectroscopic evidence for the presence of anthracene in samples of triphenylmethane, while Orndorff, Gibbs, McNulty and Shapiro[6] found similar evidence of the presence of anthracene in some of their samples of diphenylmethane. On the other hand, Zelinsky and Gawerdowskaja[7] claim that the stable form of triphenylmethane (m. p. 92°) dissolves in sulfuric acid without color and that it then changes over to the metastable form (m. p. 82°) to which they ascribe the yellow color. They were unable to detect the presence of anthracene in their samples. Evidence has been obtained in this Laboratory that color is produced when pure samples of these methanes are dissolved in sulfuric acid and that this production of color is a result of chemical reaction between solute and solvent.

Triphenylmethane is very slightly soluble in sulfuric acid.[8] The solution is colorless at first but it slowly acquires a yellow color upon standing or more quickly upon being warmed or exposed to sunlight. The absorption spectrum of one sample of the yellow solution is shown by curve 1, together with the curve 2 for pure triphenylcarbinol sulfate. It is apparent that the two curves are produced by the same substance. The curves indicate that only a portion of the triphenylmethane is converted to the carbinol sulfate; for example, in the particular experiment for which the absorption curve of the solution is given, the data indicate the formation of 0.0006 g. of triphenylcarbinol sulfate from 0.00247 g. of triphenylmethane. At-

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(1) Baeyer and Villiger, *Ber*, **35**, 1194, 1754 (1902)

(2) Ullmann, *ibid.*, **35**, 1811 (1902).

(3) Baker, *J. Chem Soc*, **91**, 1490 (1907).

(4) Massol and Faucon, *Compt rend*, **166**, 819 (1918)

(5) McVicker, Marsh and Stewart, *J. Chem. Soc.*, **127**, 999 (1925)

(6) Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49**, 1541 (1927)

(7) Zelinsky and Gawerdowskaja, *Ber*, **61**, 1049 (1928).

(8) A mixture of dimethyl sulfate and sulfuric acid constitutes a much better solvent than sulfuric acid for these hydrocarbons. It has been found that the spectra of the solutions in this mixture of solvents, at least in those cases where the concentration of dimethyl sulfate is less than 30% by volume, are identical with the spectra obtained for corresponding solutions in concentrated sulfuric acid alone The mixture of solvents has therefore been used for nearly all of the solutions discussed in this paper.

tempts were made to produce sufficient sulfate in the solution to allow the isolation of some pure carbinol. The passage of either air or oxygen through a suspension of several grams of finely powdered triphenylmethane in sulfuric acid (4 volumes) and dimethyl sulfate (1 volume) produced only slightly more color after several days than was obtained by shaking a sealed tube containing the same mixture. Only a few tenths of a gram could be recovered from four grams of triphenylmethane which went into solution. The recovered material, which was obtained by distillation of the diluted acid solution in a current of steam, melted at 81–82° and was impure triphenylmethane, as was proved by the melting point of mixtures of this material with pure triphenylmethane. It was not the metastable form of triphenylmethane since its melting point was not changed by seeding the supercooled molten mass with crystals of the 92° form. Schaum[9] has shown that the rate of change of the metastable form to the

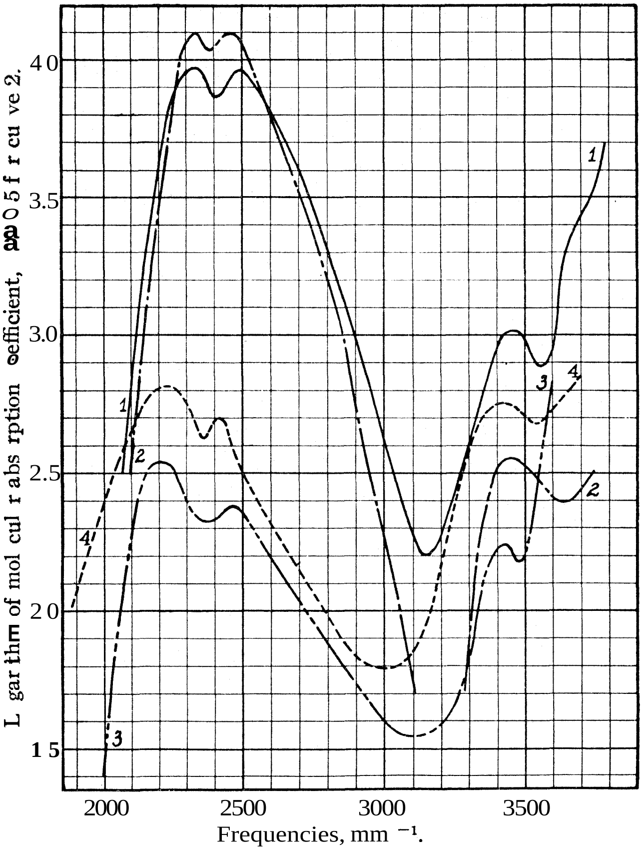

Fig. 1.

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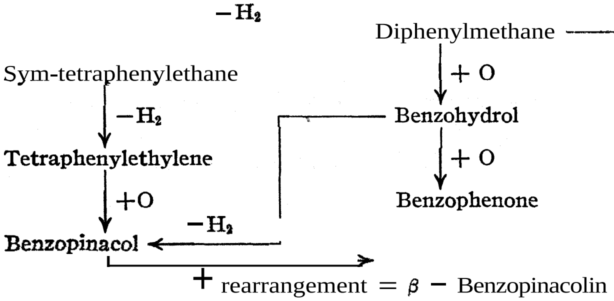
(9) Schaum, *Ann.*, **462**, 194 (1928).

stable is extremely rapid at 90°. The balance of the triphenylmethane which dissolves in sulfuric acid is probably sulfonated, as has been suggested by Ullmann.[2] Attempts to isolate the sulfonic acid have thus far been unsuccessful.

As a result of the spectroscopic data, we conclude that the color of a sulfuric acid solution of triphenylmethane is due to the presence of the sulfate of triphenylcarbinol which has been produced by the oxidation of a portion of the hydrocarbon.

The causes of the color produced in solutions of diphenylmethane in sulfuric acid are not so apparent. The following chart illustrates the more obvious ways in which oxidation of diphenylmethane might be expected to take place



The absorption spectra of sulfuric acid solutions of each of the above compounds, as well as of anthracene and anthraquinone, have been determined. These curves have been compared and it has been found that with the exception of the curve for tetraphenylethane there is no similarity between the absorption spectrum of a sulfuric acid solution of any of these compounds and that shown by the diphenylmethane solutions.

Curve 3 was obtained from a 1-cm. layer of a solution of 0.00826 g. of diphenylmethane in 25 cc. of sulfuric acid (4:1) and curve 4 from a solution of 0.00058 g. of tetraphenylethane in 25 cc. of the same solvent. The similarity of the curves leads one to believe that very similar solutions are produced when either diphenylmethane or *sym*-tetraphenylethane is dissolved in sulfuric acid. Only very dilute solutions can be obtained and it has thus far been impossible to isolate any of the products. The close relationship between derivatives of diphenylmethane and tetraphenylethane has been noted also by other investigators.[10]

The absorption curves were obtained by methods which have been described.[11] The crystalline compounds were recrystallized from anhydrous ether or optically clear petroleum ether and in every case melted sharply at temperatures close to those recorded for them. The diphenyl-

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(10) (a) Willstätter and Goldmann, Ber., 39, 3765 (1906); (b) Madelung and Oberwegner, *ibid.*, 60,2469 (1927); (c) Gilman and Leermakers, Rec. *trav. chim.*, 49,532 (1930)

(11) Anderson and Gomberg, THIS JOURNAL, 60,203 (1928).

methane was purified by treatment for thirty minutes with 85% sulfuric acid and was then distilled in a current of steam. The product gave no color with concentrated sulfuric acid until the mixture was warmed or allowed to stand for several hours.

Summary

1. Curves are presented for the absorption spectra of diphenylmethane, tetraphenylethane and triphenylmethane in solution in a mixture of sulfuric acid and dimethyl sulfate.

2. It has been shown that the color produced when triphenylmethane is dissolved in sulfuric acid is caused by the formation of triphenylcarbinol sulfate due to the oxidation of some of the triphenylmethane to triphenylcarbinol.

3. Sulfuric acid solutions of diphenylmethane give absorption spectra which are very similar to the spectra of sulfuric acid solutions of *sym*-tetraphenylethane. Whether this is due to the oxidation of diphenylmethane to a derivative of tetraphenylethane or to a cleavage of the tetraphenylethane to a diphenylmethane derivative cannot be demonstrated at present.

ANN ARBOR, MICHIGAN

RECEIVED AUGUST 17, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Tertiary Aliphatic Alcohols Containing an Adjacent Tertiary Hydrogen, the Related Chlorides and Dehydration Products

BY FRANK C. WHITMORE AND W. L. EVERS[1]

The need for more knowledge about tertiary alcohols in connection with studies on rearrangements prompted this work.[2] The group of alcohols selected may be represented by the formula, $R(CH_3)(iso\text{-}C_3H_7)COH$, in which R is ethyl, n-propyl, *n*-butyl and n-amyl. Two adjacent carbons hold tertiary hydroxyl and tertiary hydrogen. These are readily removed to give a tetrasubstituted olefin. That the dehydration does not follow this course alone has been shown repeatedly with the first member of the series in which R is methyl.[3] The dimethylisopropylcarbinol gave the expected tetramethylethylene and amounts of 2,3-dimethylbutene-1 varying with the conditions of dehydration. The second member of the

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(2) (a) Whitmore, THIS JOURNAL, **55**, 3274 (1932); (b) Whitmore and Woodburn, *ibid.*, **55**, 361 (1933); (c) Whitmore and Williams, *ibid.*, **55**, 406 (1933).

(3) Henry, *Compt. rend.*, 144, 552 (1907); Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911); Lindner, *Monatsh.*, 32, 403 (1911); Kishner and Chonin, *Chem. Zentr.*, I, 1496 (1914); *J. Russ. Phys.-Chem. Soc.*, **45**, 1770 (1913).

series, methylethylisopropylcarbinol, gave two olefins but these were not identified.[4]

The four carbinols in the present study, when dehydrated by Hibbert's iodine method, gave mainly the tetrasubstituted olefins with lesser amounts of the olefins formed by the loss of hydrogen from the R group. No evidence was found that the methyl group was involved.[2c] The structure of the olefins was determined by ozonolysis. With the n-butyl and n-amyl compounds, the olefinic products were carefully fractionated. A study of the refractive index–distillate curve indicated that the dehydrations involving the tertiary and secondary hydrogens took place in about the ratio 2 .1.

The tertiary chlorides were prepared and were found to be at least as stable as the related chlorides containing normal propyl instead of isopropyl groups.[2b,c] Thus the adjacent tertiary hydrogen had little or no greater effect than an adjacent secondary hydrogen. This is probably because the controlling step in the loss of hydrogen chloride is the removal of the chlorine with its complete octet.[2a]

Experimental

The carbinols were prepared from methyl isopropyl ketone (b. p. 91.5–92.3" (733 mm.)), n^{20}_{D} 1.3880, prepared in 60% yield by the hydrolysis and rearrangement of trimethylethylene dibromide prepared from tertiary amyl alcohol)[5] and the proper Grig-

TABLE I

THE TERTIARY CARBINOLS, R(CH_3)(ISO-C_3H_7)COH AND THEIR CHLORIDES

Carbinols

R	Wt. made, g.	Yield %	B. p., °C. (mm.)	n^{20}	d^{20}_4
C_2H_5	540	59	39– 38 (7) 44– 45 (14) 136–137 (740)[b]	1.4287	0.833
n-C_3H_7	130	35	42– 43 (6)[c]	1.4300	
n-C_4H_9	480	61	56– 57 (5) 42 (2)	1.4365	.8395[d]
n-C_5H_{11}	420	60	69– 70 (5)	1.4380	.8401

Chlorides

R	Wt. made, g.	Yield %	B. p., °C. (mm.)	n^{20}_{D}	d^{20}_4	Analysis, % Cl		
						Calcd.	Found	
C_2H_5	20	50[a]	133–138			26.3	24.3	24.4[a]
n-C_3H_7	24	81	41– 43 (12)	1.4350	0.8869	23.9	23.3	23.4
n-C_4H_9	56	86	54 (8)	1.4391	.885[e]	21.8	21.2	21.8
n-C_5H_{11}	33	77	53– 55 (3)	1.4420	.8818	20.1	20.1	19.8

[a] The low yield and the low chlorine content were due to a slight decomposition during the distillation at atmospheric pressure. [b] Chavanne and de Graef (Ref. 4b) give b. p. 42–43° (11 mm.), and 139.4–139.9° (760 mm.). [c] Clarke [THIS JOURNAL, **33,** 528 (1911)] gives b. p. 158–158.2° (758 mm.). [d] d^{21}_4 0.8383. [e] Calcd. from d^{23}_4 0.8809.

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[4] (a) Pariselle and Simon, *Compt. rend.*, 173, 86 (1921); (b) Chavanne and de Graef, *Bull. soc. chim. Belg.*, **33,** *366* **(1924).**

[5] Supplied by the Sharples Solvents Corp. of Philadelphia.

nard reagents. The halides used for their preparation were n-amyl bromide, b. p. 126.5–128° (740 mm.), prepared in 58% yield from n-amyl alcohol[6] and constant boiling hydrobromic acid; n-butyl bromide, b. p. 99–100° (740 mm.); n-propyl bromide, b. p. 68.5–70° (730 mm.) and ethyl bromide (Dow Chemical Co.).

The ethyl compound was also made from isopropyl bromide (b. p. 58–59° (740 mm.), prepared in 78% yields from 98% isopropyl alcohol[6] and constant boiling hydrobromic acid) and methyl ethyl ketone, b. p. 79–79.5° (739 mm.), prepared by dehydrogenating, with a brass catalyst, secondary butyl alcohol[6] (b. p. 97.7–98.7° (733 mm.)). The yield of tertiary carbinol was only 33%, probably due to the condensing action of the isopropyl Grignard on the ketone.[4a,7]

The tertiary chlorides were prepared from the carbinols in the usual way with dry hydrogen chloride at 0°. This treatment gave colorless or slightly yellow crude chlorides in sharp difference from the behavior of the corresponding n-propyl compounds, which gave deep colors.[2b,c]

The results on the tertiary carbinols and halides are summarized in Table I.

The carbinols were dehydrated by refluxing with a few crystals of iodine under a 50 X 1.5 cm. column. The olefin and water were distilled as formed. The olefin was washed with 10% sodium thiosulfate, dried over 10 g. of calcium chloride and finally over sodium. The product was then distilled through a short column.

TABLE II

DEHYDRATION OF THE CARBINOLS $R(CH_3)(iso\text{-}C_3H_7)COH$

R	Wt., g.	Water formed, g.	Olefin b. p. range, °C. (mm.)	Olefin, g.	Yield, %
C_2H_5	223	30	89–93.5 (732)	130	70
n-C_3H_7	65	7	108–115 (733)	28	50
n-C_4H_9	72	7	135–140 (742)	46	74
n-C_5H_{11}	474	46	159–166 (747)	325	77

The olefins were ozonized in about 0.3-mole lots in 250 cc. of 5–35° saturated hydrocarbons[8] at 0° in the usual way? The ozonides were decomposed with zinc and hot water.[9] The results appear in Table III.

The ozonolysis products indicate that the dehydration took place exclusively from the isopropyl and R groups with the former predominating about 2:1. The carbinols gave the following pairs of olefins: ethylmethylisopropylcarbinol, 2,3-dimethylpentene-2 and -3; n-propylmethylisopropylcarbinol, 2,3-dimethylhexene-2 and -3; *n*-butylmethylisopropylcarbinol, 2,3-dimethylheptene-2 and -3; n-amylmethylisopropylcarbinol, 2,3-dimethyloctene-2 and -3.

Two of the pairs of olefins, those from the n-butyl and the n-amyl carbinols, were carefully fractionated through a 130 X 1.5 cm. adiabatic, total condensation variable reflux packed column,[10] using a reflux ratio of about 20:1.

The distillation of 320 g. of the olefins from n-butylmethylisopropylcarbinol gave 32 fractions of which the principal ones were 3–11, 112 g., b. p. 135.4° (743 mm.) to 137.1° (741 mm.), n^{20}_{D} 1.4232 to 1.4236; and 19–23, 42.5 g., b. p. 138.2–139.0° (741 mm.), n^{20}_{D} 1.4246–1.4257. These results taken with the ozonolysis results and the studies of Boord and his co-workers[11] indicate that the olefin formed in larger amount is the heptene-2 derivative. Measurements on the middle fractions of the olefins gave the follow-

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(6) Supplied by Stanco, Inc., New York City.

(7) Conant and Blatt, THIS JOURNAL, 51, 1227 (1929).

(8) Supplied by the Viking Corp. of Charleston, W. Va.

(9) See Whitmore and Church, THIS JOURNAL, 54, 3712 (1932).

(10) Table III, Ref. b.

(11) Schmitt and Boord, THIS JOURNAL, 54, 751 (1932).

TABLE III

OZONOLYSIS OF OLEFINS FROM THE CARBINOLS, $R(CH_3)(iso\text{-}C_3H_7)COH$

R	Olefin used, g.	Substance in trap[a]	Substance in water layer	Oil layer, g.	No. of fractions	Fractionation of oil layer[b] chief fractions No.	B. p., °C.	g.	Substances identified	M. p., °C.
C_2H_5	49	CH_3CHO[c] No HCHO	Acetone[e]	25	11	1	−30	1.2	Acetaldehyde	
						2	55–65	1	Acetone[e]	
						7–8	90–94	5	Methyl isopropyl ketone semicarbazone	113–114.5
n-C_3H_7	28	No HCHO	Propionaldehyde Acetone	20	7	1	46–49	0.5	Propionaldehyde (skatol)[d]	
						3	76–94	5.0	Methyl isopropyl ketone semicarbazone	111–112
						4	94–104	4.5	Methyl propyl ketone semicarbazone	105–106
n-C_4H_9	31	No HCHO	Acetone	25	8	4	90–93	2	Methyl isopropyl ketone semicarbazone	112–112.4
						7	125–130	2	Methyl *n*-butyl ketone semicarbazone	117.5–118
n-C_5H_{11}	42	No HCHO	Acetone higher aldehyde	36	14	1–2	32–55	1.5	Acetone[e]	
						6–7	89–94	4.5	Methyl isopropyl ketone semicarbazone	112–113
						8–10	94–103	10	*n*-Valeraldehyde oxime	50.7–51.5
						12–14	144–152	8.5	Methyl *n*-amyl ketone semicarbazone	121–122.5

[a] A trap containing dry ether kept at 0° was placed at the end of the apparatus to catch any formaldehyde.

[b] The fractionation was by means of a 60 × 1.2 cm. adiabatic total condensation variable take-off column packed with 5 × 5 mm. glass rings; *cf.* Whitmore and Lux, THIS JOURNAL, **54,** 3451 (1932).

[c] Caught in 0° trap during decomposition of ozonide. Identified by conversion to ethylidene β-naphthol oxide, m. p. 172–174°.

[d] Tested with phenylhydrazine according to Mulliken.

[e] Acetone was tested with sodium nitroprusside according to Mulliken using blank tests.

ing properties: 2,3-dimethylheptene-2, b. p. 136.2–136.8° (743 mm.), n^{20}_{D} 1.4233, d^{20}_{4} 0.742; 2,3-dimethylheptene-3, b. p. 138.4–138.8" (740.5 mm.), n^{20}_{D} 1.4250, d^{20}_{4} 0.747.

Similarly 325 g. of the mixture of olefins from n-amylmethylisopropylcarbinol was distilled in 34 fractions of which the chief ones were 1–8, 72 g., b. p. 157.6° (731 mm.) to 160.2° (737.5 mm.), n^{20}_{D} 1.4280 to 1.4282; and 14–18, 45 g., b. p. 161.0° (739 mm.) to 161.8" (739.6 mm.), n^{20}_{D} 1.4289 to 1.4292. The lower boiling olefin was taken as the octene-2 derivative. The middle fractions gave the following properties: 2,3-dimethyloctene-2, b. p. 158.4–158.8° (733 mm.), n^{20}_{D} 1.4280; 2,3-dimethyloctene-3, b. p. 161.2–161.4° (739 mm.), n^{20}_{D} 1.4290.

Summary

1. Aliphatic alcohols containing tertiary hydroxyl and tertiary hydrogen on adjacent carbon atoms have been prepared and dehydrated. In each case a pair of olefins was formed. These were identified by ozonolysis.
2. The new tertiary alcohols prepared and studied were 2,3-dimethylhexanol-3, 2,3-dimethylheptanol-3 and 2,3-dimethyloctanol-3.
3. These alcohols were converted to the corresponding tertiary chlorides, 3-chloro-2,3-dimethyl-hexane, -heptane and -octane.
4. The four olefins, 2,3-dimethylheptene-2 and -3 and 2,3-dimethyloctene-2 and -3 have been prepared and studied.

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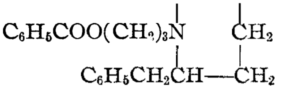
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

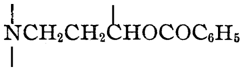
Piperidine Derivatives. XII. Local Anesthetics Derived from Reduction Products of Beta-Acetylpyridine

BY FRANK M. STRONG AND S. M. MCELVAIN

Two constructions that markedly enhance the action of the aminoalkyl benzoate type of local anesthetics on mucous surfaces have been shown to be (a) the phenylalkyl group attached to nitrogen[1] (preferably the nitrogen atom of the piperidine ring) and (b) a substituent methyl group in the alkylene group that joins the nitrogen atom to the benzoyloxy group.[2] These two types of structure are illustrated by I and II. It was the purpose of the work reported in the present paper to prepare and submit for pharmacological study a series of compounds of type III in which the two above-mentioned structures might be combined in a single molecule.

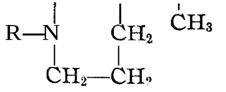


I



$-\overset{|}{\underset{|}{N}}CH_2CH_2\overset{CH_3}{\overset{|}{C}}HOCOC_6H_5$

II



III

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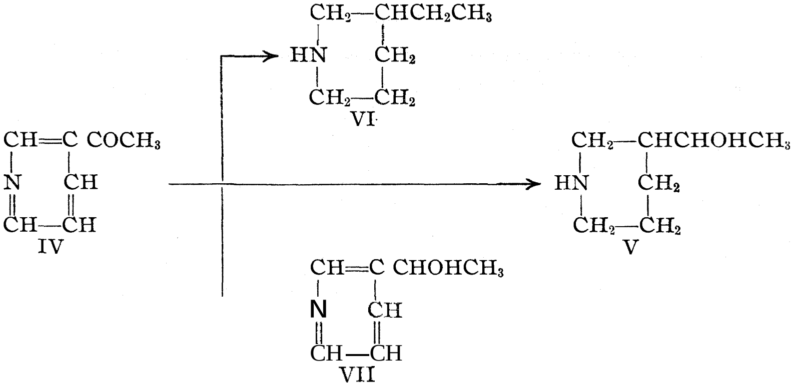
(1) (a) Bailey and McElvain, THIS JOURNAL, 52, 1639 (1930); (b) Bolyard and McElvain, *ibid.*, 51, 927 (1929).

(2) Thayer and McElvain, *ibid.*, 50, 3354 (1928)

The synthesis of this type of compound was accomplished by first alkylating and then benzoylating 3-piperidylmethylcarbinol (V) which was obtained by the reduction of β-acetylpyridine (IV). This reduction was carried out catalytically with both Adams platinum oxide catalyst and a nickel catalyst and also by sodium in alcohol. Each of these reduction procedures gave a mixture of the diastereoisomeric carbinols (V) together with a relatively large amount of 3-ethylpiperidine (VI). Since the reduction with the platinum catalyst seemed to be most satisfactory from the standpoint of control and yield of the desired product, the results obtained by this method will be outlined briefly. When the ketone (IV) was reduced in dilute hydrochloric acid solution with the platinum catalyst and the reduction stopped after 4 moles of hydrogen had been absorbed, a small amount of the partially reduced product, β-pyridylmethylcarbinol VII was isolated along with V and VI.



If, however, the reduction were allowed to proceed until no more hydrogen was absorbed, only V and VI were isolated. The yields of these latter products were 38–52% and 30–38%, respectively. In aqueous solution containing no hydrochloric acid the ketone IV absorbed only one mole of hydrogen and from this reduction the carbinol VII was isolated in 85% yield. Apparently the formation of a small amount of the more basic piperidine compound destroyed the activity of the catalyst, because the addition of hydrochloric acid to the solution after the one mole of hydrogen had been absorbed allowed the reduction to continue to completion. The reduction of VII either with platinum or nickel catalysts produced both V and VI in the relative amounts mentioned above.[3] Reduction of either this carbinol or β-acetylpyridine by sodium and alcohol produced even higher ratios of ethylpiperidine.

(3) This fact is in accord with the observations of Adkins and co-workers in this Laboratory that a carbinol group attached to an unsaturated carbon atom is converted to a methylene group by catalytic reduction with nickel. Also there is an apparent correlation between the behavior of β-acetylpyridine and β-benzoylpyridine on reduction with platinum In the reduction of the three benzoylpyridines it was only in the case of the 0-compound that a low yield of the phenylpiperidylcarbinol was obtained [Crook and McElvain, THIS JOURNAL, 52,4011 **(1930)**].

The mixture of the isomeric 3-piperidylmethylcarbinols (V) which was obtained consisted of approximately 20% of a higher melting (103–104°) compound and 80% of a lower melting (58–61°) compound. In spite of this adverse ratio the higher melting compound was used in the subsequent experiments because lower solubility caused it to be much more susceptible to purification. The relationship between these two compounds was established by analysis and acetyl value.[4] Attempts to convert the lower melting isomer into the higher melting one as was done in the case of the 2-piperidylphenylcarbinols[4] were unsuccessful.

A number of N-alkyl and N-phenylalkyl derivatives of the higher melting 3-piperidylmethylcarbinol were prepared and benzoylated and the desired anesthetics (type III) obtained as the hydrochlorides without any particular difficulty. The N-benzoyloxypropyl derivative of ethylpiperidine was prepared for comparison with previously prepared alkylpiperidinopropyl benzoates. Also the β-pyridylmethylcarbinol (VII) was converted into the benzoate and *p*-aminobenzoate, both of which, as will be seen from the pharmacological data, were found to possess very unusual physiological properties.

Experimental

Ethyl Nicotinoacetate Hydrochloride.—The free base of this compound has been prepared, but not isolated or purified, by Hurd.[5] The following procedure was used in the present work. A mixture of 151 g. (1 mole) of ethyl nicotinate, 167 g. (1.9 moles) of ethyl acetate and 104 g. (1.55 moles) of sodium ethoxide was allowed to stand at room temperature for about one hour with occasional shaking. The mixture became quite warm and assumed a deep reddish brown color. It was then refluxed five to six hours, cooled and diluted with an equal volume of water. The unreacted esters were extracted with ether and the remaining aqueous solution acidified with concentrated hydrochloric acid and then made slightly alkaline with sodium carbonate solution. The oily layer of ethyl nicotinoacetate and acetoacetic ester was separated and the aqueous layer extracted twice with ether. These ether extracts were combined with the keto ester layer and, after drying with anhydrous potassium carbonate, saturated with dry hydrogen chloride. The precipitated ethyl nicotinoacetate hydrochloride after recrystallization from an alcohol–ether mixture melted at 156–157.5°. The yield was 115–161 g. (50–70%). Calcd. for $C_{10}H_{12}O_3NCl$: Cl, 15.44. Found: Cl, 15.39.

β-Acetylpyridine Hydrochloride.—A solution of 42 g. of ethyl nicotinoacetate in 300 cc of 10% hydrochloric acid was refluxed for six hours. The resultant solution, which gave no coloration with ferric chloride, was evaporated to dryness on a steam-bath and the remaining residue recrystallized from alcohol. A yield of 27 5 g. (96%) of β-acetylpyridine hydrochloride, m. p. 176–177.5°, was obtained Calcd. for C_7H_8ONCl: Cl, 22.51. Found: Cl, 22.69.

The free base boils at 90–92° (5 mm.), melts at 13–14', and is completely soluble in cold water.

β-Pyridylmethylcarbinol, 3-Piperidylmethylcarbinol (2 Forms) and 3-Ethylpiperidine.—A solution of 25 g. of β-acetylpyridine in 150 cc. of distilled water was shaken with 0.5 g. of Adams platinum oxide catalyst until no more hydrogen was absorbed. At this point approximately one mole of hydrogen had been taken up, and if the catalyst

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(4) Ref. 3, p. 4010.

(5) Hurd, THIS JOURNAL. 49, 551 (1927)

were removed and the solution distilled, 21.5 g. (85%) of **β-pyridylmethylcarbinol**,[6] b. p. 123–125° (5 mm.), was obtained.

Anal. Calcd. for C_7H_9ON: C, 68.3; H, 7.32, acetyl value,[4] 1. Found: C, 68.2; H, 7.49; ac. v., 0.96. The hydrochloride of this carbinol melts at 92–93°. Calcd. for $C_7H_{10}ONCl$: Cl, 22.25. Found: Cl, 22.20.

If, however, 20 cc. of hydrochloric acid (sp. gr. 1.2) were added to the reduction mixture after the first mole of hydrogen had been absorbed and the reduction allowed to continue, the total hydrogen absorption amounted to about 10% excess of 4 moles. It was necessary toward the end of the reduction to reactivate the catalyst by shaking with oxygen. The catalyst was then filtered off and the filtrate evaporated to dryness. The residue was taken up in absolute alcohol and titrated with alcoholic potassium hydroxide using phenolphthalein as an indicator. The precipitated potassium chloride was filtered off and, after removal of the alcohol, the free bases were fractionated. Yields of 7–9 g. (30–38%) of 3-ethylpiperidine[7] b. p. 148–152°, and 10–14 g. (38–52%) of material boiling at 105–120° (3 mm.), which on cooling solidified, were obtained. This solid was extracted with 50 cc. of boiling absolute ether and the ethereal solution filtered. After three such extractions and filtrations a residue of the higher melting isomer, m. p. 103–104°, remained. The yield of this isomer amounted to 2–2.5 g. Calcd. for $C_7H_{15}ON$: C, 65.2; H, 11.70; acetyl value 2. Found: C, 64.9; H, 11.70; ac. v., 1.91. The hydrochloride of this isomer melted at 152–153°. Calcd. for $C_7H_{16}ONCl$: Cl, 21.45. Found: Cl, 21.17.

The ethereal extracts obtained above were saved and several of them worked up together. After removal of the ether by distillation, the remaining residue was distilled. It boiled at 116–119° (5 mm.) and solidified on cooling. A 16.5-g. sample recrystallized from dioxane yielded 10 g. of material, m. p. 56–60". The melting point of this compound could be raised to 58–61" by further recrystallizations. Calcd. for $C_7H_{15}ON$: C, 65.2; H, 11.70; acetyl value, 2. Found: C, 65.1; H, 11.62; ac. v., 1.99. This isomer gave a hydrochloride which could not be caused to crystallize.

α-(1-Alkyl-3-piperidyl)-ethyl Benzoate Hydrochlorides.—These compounds were prepared by first heating 2 moles of the higher melting 3-piperidylmethylcarbinol with 1 mole of the appropriate alkyl halide in dioxane solution for a few hours on a steam-bath. After cooling, the reaction mixture was diluted with absolute ether and the precipitated carbinol hydrohalide filtered off. The solvent was removed from the filtrate by distillation and the residue warmed with a 30% excess of benzoyl chloride. The resulting reaction mixture was diluted with ether, the precipitated hydrochloride taken up in absolute alcohol and caused to crystallize by the careful addition of ether. The compounds which were prepared are summarized in Table I. The phenylbutyl derivative is omitted because no crystalline salt could be prepared from it.

TABLE I

α-(1-ALKYL-3-PIPERIDYL)-ETHYL BENZOATE HYDROCHLORIDES

Compound Type III R is	Formula	M. p., °C.	Analyses, Cl, % Calcd.	Found
Benzyl	$C_{21}H_{26}O_2NCl$	199–200	9.86	9.88
8-Phenylethyl	$C_{22}H_{28}O_2NCl$	196–198	9.49	9.52
y-Phenylpropyl	$C_{23}H_{30}O_2NCl$	158–159	9.16	9.14
ε-Phenylamyl	$C_{25}H_{34}O_2NCl$	141–142	8.55	8.65
n-Hexyl	$C_{20}H_{32}O_2NCl$	142–144	10.04	10.07

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[6] This compound has been imperfectly described by Hardy and Calmels, *Bull. soc. chim.*, 48, 230 (1887).

[7] The hydrochloride melted at 140–141°; cf. Günther, *Ber.*, 31, 2140 (1898). The acetyl value[4] of the free base was 1.03.

γ-(3-Ethylpiperidino)-propyl Benzoate Hydrochloride.—This compound was preprepared from 3-ethylpiperidine and chloropropyl benzoate by a procedure previously described.[8] It melted at 164–165°. Calcd. for $C_{17}H_{26}O_2NCl$: Cl, 11.38. Found: Cl, 11.33.

The Hydrochloride of **α-(β-Pyridyl)-ethyl** Benzoate **and *p*-Nitrobenzoate.**—β-Pyridylmethylcarbinol was benzoylated by mixing with a slight excess of benzoyl chloride and allowing to stand at room temperature. The reaction mixture became very hot and darkened considerably. On cooling it solidified. The resultant mass was recrystallized from an alcohol–ether mixture. The yield of α-(β-pyridyl)-ethyl benzoate hydrochloride, m. p. 175–176°, was 85% of the theoretical. Calcd. for $C_{14}H_{14}O_2NCl$: Cl, 13.47. Found: Cl, 13.40.

The p-nitrobenzoate hydrochloride was prepared by heating the carbinol with *p*-nitrobenzoyl chloride in benzene solution for four to five hours. The precipitated hydrochloride after recrystallization from alcohol melted at 199–200°. Calcd. for $C_{14}H_{13}O_4N_2Cl$: Cl, 11.50. Found: Cl, 11.37.

α-(β-Pyridyl)-ethyl *p*-Aminobenzoate.—The catalytic reduction of the above p-nitrobenzoate was unsuccessful, presumably on account of simultaneous reduction of the pyridine ring. However, it was readily reduced to the p-aminobenzoate in 75% yields by iron powder and dilute hydrochloric acid. No crystalline salt of this compound could be obtained so it was purified by distillation and recrystallization. It boiled at 227–230° (4 mm.) and, after recrystallization of the distillate from dilute alcohol, it melted at 100–101°. Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.4; H, 5.82; N, 11.57. Found: C, 69.7; H, 5.73; N, 11.38.

Pharmacological Report

The local anesthetics prepared in the course of this work are being studied pharmacologically by Dr. K. K. Chen and Mr. Charles L. Rose of The Lilly Research Laboratories, Indianapolis, Indiana. A preliminary report on the pharmacological properties of these compounds is summarized in Table II.

The durations of anesthesia were determined in the usual way by application of a 1% solution of the anesthetic to a rabbit's cornea. Toxicities are reported as subcutaneous to white mice and intravenous to white rats.

TABLE II

PHARMACOLOGICAL DATA

Compound	Av. duration of corneal anesthesia, Min.	% soln.	Subcutaneous toxicity (mg. kg.) M. L. D.	Intravenous toxicity (mg. kg.) M. L. D.
Benzyl	68	1	200	10
β-Phenylethyl	40	1	1000	35
y-Phenylpropyl	83	1	1000	45
γ-Phenylamyl	180	1		40
n-Hexyl	72	1	1000	32
VIII	15	1	1000	30
IX	43	1	1000	100
X	0	1	. .	110
Cocaine	29	2	150	17.5
Procaine	0	2	1000	40

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[8] McElvain, THIS JOURNAL, **49**, 2837 (1927).

The benzoates of α-(1-alkyl-3-piperidyl)-ethyl alcohols are designated in Table II by the substituent alkyl groups as in Table I. γ-(3-Ethylpiperidino)-propyl benzoate, α-(β-pyridyl)-ethyl benzoate and α-(β-pyridyl)-ethyl *p*-aminobenzoate are designated by the numerals VIII, IX and X, respectively. Since the latter compound was furnished as the free base, it was put into solution by titration with one equivalent of hydrochloric acid. Cocaine and procaine are included in the table for comparison.

Discussion of the Pharmacological Data

It is seen from the above data that the phenyl alkyl substituents in this type of structure produce anesthetics of relatively high potency. It should be noted, however, that the highest value is obtained with the phenylamyl derivative, a fact which fails to agree with the previous observation''' that maximum anesthetic effects were produced when the phenyl radical was attached to the nitrogen atom by less than five carbon atoms. Also a comparison of the anesthetic activity of the phenylethyl derivative in the above table with 1-phenylethyl-4-piperidyl benzoate[rb] indicates that the substituent methyl group in the carbon chain between the nitrogen atom and the benzoyloxy group decreases rather than increases the anesthetic activity of the compound.

The 3-ethylpiperidinopropyl benzoate (VIII) shows approximately the same order of pharmacological activity as the corresponding methylpiperidino compounds.[8]

The anesthetics derived from β-pyridylmethylcarbinol (IX and X) show the most unusual and unexpected pharmacological behavior. It is seen that the benzoate (IX) produces considerably longer anesthesia in 1% solution than does cocaine in 2% solution. At the same time its toxicity is exceedingly low, being less than half of that of procaine. However, this compound produced considerable irritation of the rabbit's eye, presumably on account of the acidity of the salt of such a weak base. It was for this reason that the corresponding *p*-aminobenzoate (X) was prepared and used as a monohydrochloride. This change in structure did not decrease the irritating qualities of the compound but it did completely destroy its anesthetic action on mucous surfaces. The *p*-aminobenzoate did, however, produce considerable anesthetic effect when injected intracutaneously. Its most surprising property was the extremely low intravenous toxicity, which was found to be even less than that of the benzoate. The pharmacological behavior of this compound is completely out of line with past observations.[9] These have definitely pointed to the generalization that \$-aminobenzoates produce at least as much anesthetic effect as the corresponding benzoates and are generally considerably more toxic.

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(9) In agreement with this behavior, however, is the recorded experiment [Ehrlich and Einhorn, Ber., **27**, 1870 (1894)] that the introduction of an amino group into the benzoyl radical of cocaine causes inactivation.

Summary

The following reduction products have been isolated from the catalytic reduction of β-acetylpyridine: ethylpiperidine, two diastereoisomeric forms of 3-piperidylmethylcarbinol and β-pyridylmethylcarbinol.

A group of new local anesthetics has been prepared from these reduction products. The data which are presented show that these anesthetics, particularly those derived from @-pyridylcarbinol, possess unusual and interesting pharmacological properties.

MADISON, WISCONSIN
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]

Organic Selenium Compounds. II. A New Type of Aromatic Selenium Halide

BY DUNCAN G. FOSTER

Introduction

There are, at the present time, four types of organic selenium halides described in the literature: (1) $RSeX$, in which R is aromatic; (2) $RR'SeX_2$, in which R and R' are either di-aryl or alkyl-aryl; (3) R_3SeX, in which R is aryl only; and (4) $RSeX_3$. The only reported case of this last type is Shaw and Reid's ethyl selenium tribromide, $C_2H_5SeBr_3$,[1] no aromatic compounds of this type and no analogous compounds in which X is another halogen than bromine having been prepared. This list does not include halogen acid addition compounds, such as $RSeO_2H \cdot HCl$, but only true halides.

In the course of an investigation of the reactions of the first three types of halides mentioned, to'be reported in a later paper, the formation of phenyl selenium tribromide, the first example of an aromatic compound of the last-mentioned class, has been observed, the analogous phenyl selenium trichloride, $C_6H_5SeCl_3$, has also been prepared, and an unsuccessful attempt made to prepare phenyl selenium triiodide, which is too unstable to exist under ordinary conditions. The various synthetic methods employed with these compounds and some of their reactions indicate that they are halogen salts of a selenonium base, $C_6H_5Se(OH)_3$, the ortho form of ordinary benzene seleninic acid, C_6H_5SeOOH.

Outline and Discussion of the Present Investigation

(1) **Phenyl selenium tribromide,** $C_6H_5SeBr_3$, was first observed as a by-product formed during the preparation of phenyl ethyl selenium dibromide, $(C_6H_5)(C_2H_5)SeBr_2$, from phenyl ethyl selenide, $(C_6H_5)Se(C_2H_5)$

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(1) Shaw and Reid, THIS JOURNAL, 48, 525 (1926).

and bromine by the method of Edwards, Gaythwaite, Kenyon and Phillips[2] The equation for this reaction is

$$(C_6H_5)(C_2H_5)Se + Br_2 = (C_6H_5)(C_2H_5)SeBr_2 \qquad (1)$$

When the phenyl ethyl selenide was that which had been prepared by regeneration from phenyl selenium monobromide, C_6H_5SeBr, by means of magnesium and ethyl bromide (the details for this reaction are given in the Experimental Part of this paper) and when the reaction mixture was allowed to become warm from the heat of the reaction, a second product was formed, which appeared from the recrystallizing solvent as rose colored needles and was identified as $C_6H_5SeBr_3$. The explanation of its formation is probably as follows. The investigators mentioned above have shown that phenyl ethyl selenium dibromide decomposes above its melting point (86°) to phenyl selenium bromide and ethyl bromide.

$$(C_6H_5)(C_2H_5)SeBr_2 = C_6H_5SeBr + C_2H_5Br \qquad (2)$$

I have observed that this reaction also takes place slowly at room temperature and fairly rapidly even at the boiling point of ether. Thus, if, during the bromination of phenyl ethyl selenide, the mixture is not cooled, some C_6H_5SeBr will be formed. This can then react directly with bromine to form $C_6H_5SeBr_3$.

$$C_6H_5SeBr + Br_2 = C_6H_5SeBr_3 \qquad (3)$$

It is also possible that there was still some C_6H_5SeBr in the solution used, which had not been acted upon by the magnesium, and this would also be converted to $C_6H_5SeBr_3$.

Assuming that reaction **(3)** really took place, I was able to prepare phenyl selenium tribromide in good yield by treating an ether solution of C_6H_5SeBr with the calculated quantity of free bromine.

(2) **Phenyl** Selenium Trichloride, $C_6H_5SeCl_3$.—No chlorine compounds of this type have been prepared, but they should, since the bromine analog was found to be so stable, be easily capable of existence and of preparation by one of three different methods: (a) by the pyrolytic decomposition of phenyl ethyl selenium dichloride and treatment of the product with chlorine

$$(C_6H_5)(C_2H_5)SeCl_2 + \textbf{(heat)} = (C_6H_5SeCl) + C_2H_5Cl \qquad (4)$$

$$(C_6H_5SeCl) + Cl_2 = C_6H_5SeCl_3 \qquad (5)$$

(b) by the displacement with chlorine of the bromine in $C_6H_5SeBr_3$

$$2C_6H_5SeBr_3 + 3Cl_2 = 2C_6H_5SeCl_2 + 3Br_2 \qquad (6)$$

and (c) by the action of chlorine on C_6H_5SeBr

$$2C_6H_5SeBr + 3Cl_2 = 2C_6H_5SeCl_3 + Br_2 \qquad (7)$$

All of these reactions were tried and all gave good yields of the rather unstable, pale yellow solid, $C_6H_5SeCl_3$.

(2) Edwards, Gaythwaite Kenyon and Phillips, J. *Chem.* Soc., 2302 (1928)

A fourth possible reaction, that of thionyl chloride on benzene seleninic acid, failed to give the same product

$$C_6H_5SeOOH + 2SOCl_2 = C_6H_5SeCl_3 + HCl + 2SO_2 \qquad (8)$$

(3) Attempted Preparation of Phenyl Selenium Triiodide, $C_6H_5SeI_3$.—Iodides of the type R_2SeI_2 have been described by Edwards, Gaythwaite, Kenyon and Phillips,[2] and those of the type R_3SeI by Leicester and Bergstrom.[3] Both were prepared by the action of soluble iodide (KI) on water solutions of other halides. Potassium iodide solution was therefore added to a water solution of $C_6H_5SeBr_3$. A brown precipitate formed which decomposed within ten seconds leaving an oil which appeared to contain free iodine. Potassium iodide also reacted with $(C_6H_5)(C_2H_5)SeBr_2$, but the product was a dark oil with the odor of phenyl ethyl selenide. Free iodine was without action on organic solutions of $C_6H_5SeC_2H_5$. It seemed obvious from these experiments that phenyl selenium triiodide can have no more than a transient existence under ordinary laboratory conditions.

(4) Properties of the **Trihalides.**—Phenyl selenium tribromide, m. p. 105–106°, is a rose-red solid crystallizing in circular clumps of fine needles. It is moderately soluble in all the ordinary organic solvents except ether, petroleum ether and carbon disulfide, in which it is sparingly soluble. The solutions are brownish-red, evolve bromine at the boiling point, and, on long standing, hydrogen bromide. The residue, after removal of the solvent, is a dark oil not identified. The dry substance decomposes slowly on standing, its melting point dropping, but no definite product has been identified. The substance is very soluble in water to give a *completely colorless* solution, from which all the bromine can be precipitated by silver nitrate. It is completely stable in water. A solution which stood for more than a week evolved no hydrogen bromide, but all the water evaporated, and unchanged $C_6H_5SeBr_3$ remained. The compound has a faint disgusting odor.

Phenyl selenium trichloride is a pale yellow solid, m. p. 133–144°, probably white when perfectly pure, crystallizing in short fat prisms. It is much less stable than the tribromide, becoming gummy in a few minutes with loss of hydrogen chloride and chlorine in contact with the air. It can be kept under concd. hydrochloric acid or in a desiccator in an atmosphere of hydrogen chloride gas or of chlorine. Its solubility is similar to the tribromide, organic solutions being pale yellow and the water solution colorless. It also apparently does not hydrolyze. A small quantity on a watch glass stood in contact with water for several days. At first it dissolved until saturated. The residue changed to an oil and an oil was left when the water evaporated, the same behavior it exhibited when standing alone in a desiccator. There was no sign of C_6H_5SeOOH, which would be expected to be the hydrolysis product and which is rather spar-

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(3) Leicester and Bergstrom, THIS JOURNAL, 63, 4433 (1931).

ingly soluble. The trichloride is almost odorless and all three chlorine atoms can be precipitated by silver nitrate from water solution.

These trihalides might be expected to be the acyl halides of the ortho form of benzene seleninic acid, $C_6H_5Se(OH)_3$. They do not, however, behave like acyl halides of an acid as strong as benzene seleninic, nor do they seem to be formed by reactions which would be expected to give benzene seleninyl chloride. It can be said, at least, that the action of thionyl chloride and of phosphorus pentachloride on C_6H_5SeOOH and on $C_6H_5SeOONa$, respectively, does not yield benzene selenium trichloride, but gives mixtures of solids melting over a rather broad range much higher than the melting point of $C_6H_5SeCl_3$ (in the neighborhood of 170°). Jackson[4] also treated *benzyl* seleninic acid with phosphorus pentachloride, but he did not investigate the product, so there is no way of knowing whether or not it was a trichloride. Although we have seen that neither trihalide hydrolyzes in water, as acyl halides would be expected to do, yet treatment of either with one equivalent of sodium hydroxide does produce benzene seleninic acid

$$C_6H_5SeX_3 + 3NaOH = C_6H_5SeOOH + H_2O + 3NaX \qquad (9)$$

It seemed possible that solutions of benzene seleninic acid might contain $C_6H_5Se(OH)_3$, formed by the addition of one molecule of water to the acid, which would then ionize as a base to give $C_6H_5Se^{+++}$ and 3 OH^-. If this were true, it should be possible to prepare the trihalides by the action of aqueous hydrohalogen acids on benzene seleninic acid. Some difficulty was presented by the fact that these halides are so very soluble, while the acid is only sparingly so. However, by using a large excess of ammonium bromide to provide a common ion for mass action effect, in the one case, and in the other by saturating the solution with hydrogen chloride gas, good yields of both trihalides have been obtained from C_6H_5SeOOH solution and aqueous hydrogen bromide or hydrogen chloride.

$$C_6H_5SeOOH + 3HX = C_6H_5SeX_3 + 2H_2O \qquad (10)$$

This was also the manner in which Shaw and Reid[1] obtained ethyl selenium tribromide. The inference is that ortho benzene seleninic acid is a base, and if this is true the well-known acid addition products of this acid, like $C_6H_5SeOOH{\cdot}HNO_3$, would more properly be written as true *salts*, with a molecule of water of crystallization, *e. g.*, $C_6H_5SeONO_3{\cdot}H_2O$, or as basic *salts*, $C_6H_5Se(NO_3)(OH)_2$.

Experimental Part

I. Materials

Phenyl Ethyl Selenide, $C_6H_5SeC_2H_5$.—This substance was prepared by the method described in the first paper of this series,[5] and also by the Grignard reaction, without isolating selenophenol, as follows. $C_6H_5SeMgBr$ was made from 157 g. of bromobenzene,

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[4] Jackson. *Ann.*, 179, 14 (1875).

[5] Foster and Brown, THIS JOURNAL, 60, 1184 (1928).

24 g. of magnesium and 79 g. of selenium powder in the usual manner.[6] To the ether solution obtained was added from a dropping funnel 156 g. of ethyl iodide or 109 g. of ethyl bromide mixed with an equal volume of absolute ether. The mixture was refluxed on a water-bath for one hour, then decomposed with ice and hydrochloric acid in the usual manner and the ether layer separated. The solution was washed with a total of 60 g. of sodium hydroxide in 200 cc. of water, in three portions. By acidification and extraction with ether, some selenophenol could be recovered from this extract The main ethereal solution was dried over calcium chloride, the ether distilled off and the residue distilled. The fraction boiling at 215–216° was collected as phenyl ethyl selenide. There were obtained 85 g. or 46% of the theoretical amount, also 25 g. of products boiling between 300 and 305°, which was mainly diphenyl selenide, and from the alkaline extracts 16 g. of selenophenol. The total yield of all products was 77%. Since all the products were of use, this compares favorably with the other method mentioned and saves much time.

$$C_6H_5SeMgBr + C_2H_5Br = C_6H_5SeC_2H_5 + MgBr_2 \qquad (11)$$

Phenyl Ethyl Selenium Dibromide, $(C_6H_5)(C_2H_5)SeBr_2$, was prepared by the action of bromine on phenyl ethyl selenide.[2] When this compound was recrystallized from ether it was reddish-yellow and had a melting point of 81°. From carbon tetrachloride–petroleum ether mixture it gave lemon yellow prisms, m. p. 81–83°, if melted slowly, giving a red liquid that did not solidify on cooling. If heated rather rapidly it melted sharply at 86° to give a yellow liquid that solidified on cooling. The sample investigated by Edwards, Kenyon, Gaythwaite and Phillips must have contained a small amount of the decomposition product, C_6H_5SeBr, accounting for the slightly lower melting point (81°) and reddish color which they report.

This compound was analyzed by dissolving in dilute nitric acid (5 cc. of concd. in 100 cc. of water) and precipitating with silver nitrate, and also by fusion in a Parr bomb.

Anal. I (HNO_3 method) Calcd. for 1 atom Br in $C_8H_{10}SeBr_2$: 23.18. Found: Br, 22.69. II (Parr bomb) Calcd. for total Br in $C_8H_{10}SeBr_2$: 46.36. Found: Br, 46.32.

These results show that only one of the two bromine atoms dissociates in water.

Phenyl Ethyl Selenium Dibromide from Phenyl Selenium Monobromide.—Since phenyl ethyl selenium dibromide decomposes on standing (Reaction 2), it was desirable to find a satisfactory method of recovering it. This was readily accomplished as follows: 25 g. of the decomposition product, C_6H_5SeBr, was dissolved in 100 cc. of absolute ether and 15 g. (50% excess) of ethyl bromide added; 2.5 g. of magnesium powder and a pinch of magnesium-copper couple were dropped in. After gentle warming, the ether refluxed spontaneously. When the reaction had subsided, the mixture was refluxed for two hours, until the dark red color had disappeared. It was then shaken with an equal volume of ice and saturated ammonium chloride solution, separated and dried over calcium chloride. When a few drops of this solution were evaporated on a watch glass, a liquid with the characteristic odor of phenyl ethyl selenide remained

$$C_6H_5SeBr + Mg + C_2H_5Br = C_6H_5SeC_2H_5 + MgBr_2 \qquad (12)$$

This ether solution was filtered and treated with a slight excess of bromine in the usual manner. The resultant yellow solid was filtered off and recrystallized from carbon tetrachloride–petroleum ether mixture (3–1); 3 g. of $C_6H_5SeBr_3$ and 32 g. or 89% of the theoretical quantity of $(C_6H_5)(C_2H_5)SeBr_2$ were obtained; m. p. of the latter, 85–86°. Mixed m. p. with a sample made as described in the previous paragraph, 84–85°.

Phenyl ethyl selenium dichloride, $(C_6H_5)(C_2H_5)SeCl_2$, was prepared by the method described in the earlier paper.[7]

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(6) Taboury, *Ann. chim. phys.*, **15**, 6 (1908).

(7) Ref. 5, p. 1187.

Benzene seleninic acid was prepared as described by Pyman.[8]

Phenyl selenium bromide, C_6H_5SeBr, results from the decomposition of phenyl ethyl selenium dibromide on standing, boiling for five to eight hours in ether or carbon tetrachloride, or heating just above the melting point.[2]

II. Preparation of Phenyl Selenium Trihalides, $C_6H_5SeX_3$

1. Phenyl Selenium Tribromide, $C_6H_5SeBr_3$.—(a) The substance appeared as a by-product in the preparation of phenyl ethyl selenium dibromide described in the foregoing section; rose-red needles, m. p. 105–106°. Analysis was accomplished simply by dissolving a sample in water and 5 cc. of dilute nitric acid and precipitating the bromine with silver nitrate.

Anal. Calcd. for $C_6H_5SeBr_3$: Br, 60.0. Found: Br, 60.4.

(b) From Phenyl Selenium Monobromide.—Thirteen grams of C_6H_5SeBr was dissolved in 50 cc. of dry ether and 9 grams of bromine dissolved in 20 cc. of carbon disulfide added slowly from a dropping funnel to the mixture cooled in an ice-water bath. A red solid precipitated, which was filtered off, washed with dry ether and sucked dry on the funnel; m. p. 105–106"; yield, 15.5 *g.* or 70% of the theoretical; mixed m. p. with sample described in the previous paragraph, 105–106°.

(c) From Benzene Seleninic Acid and Aqueous Hydrogen Bromide.—110 *cc.* of the mother liquor obtained in preparing C_6H_5SeOOH from its hydronitrate was used in this reaction.[8] It contained about 4 g. of C_6H_5SeOOH and 1 equivalent of ammonium nitrate; 70 g. of ammonium bromide was dissolved in it and the solution filtered free from dirt. Thirty cc. (90% excess) of constant-boiling hydrobromic acid was now added slowly. At first a yellow precipitate appeared, which rapidly turned red. The solid was filtered off, dried in a desiccator and recrystallized from carbon tetrachloride; 5.2 g. was obtained. Upon adding 50 cc. more hydrobromic acid to the filtrate, 2.8 g. more of solid was obtained; total yield, 95% of the theoretical; m. p. 105–106°; mixed m. p. with $C_6H_5SeBr_3$, 105–106°.

2. Phenyl Selenium Trichloride, $C_6H_5SeCl_3$

(a) From Phenyl Selenium Tribromide.—Five grams of $C_6H_5SeBr_3$ was dissolved in 50 cc. of dry ether and chlorine bubbled in from a tank until all the color of the liberated bromine had disappeared. Much heat was developed and the ether boiled. On cooling a yellowish granular solid came out, which was filtered off, washed rapidly with dry ether and dried in a desiccator. It was recrystallized by dissolving in boiling benzene, then cooling in ice and saturating with dry hydrogen chloride, or, by adding a little carbon disulfide to the solution, the solid slowly crystallized out in short, fat prisms without adding hydrogen chloride, but the yield was smaller; yield, 3 g. of crude material, or 91% of the theoretical; m. p. 133–134" (dec.).

Analyses were made by the same method used for the tribromide, but since the trichloride is so unstable, it was always gummy by the time it had been transferred to the weighing bottle in which it was weighed, and the analyses were always somewhat too low.

Anal. Calcd. for $C_6H_5SeCl_3$: Cl, 40.57. Found: Cl, 39.45, 39.47.

(b) From Phenyl Selenium Monobromide.—0.7 g. of C_6H_5SeBr was dissolved in about 10 cc. of dry ether in a test-tube, cooled in ice and chlorine bubbled in until saturated. A yellowish granular solid appeared. On attempting to filter, the ether caught fire spontaneously as soon as it came in contact with the air and most of the product was destroyed. About 0.2 g. was saved; m. p. 133–134° (dec.); mixed m. p. with sample obtained as in above paragraph, 133–134° (dec.).

(c) From Benzene Seleninic Acid and Aqueous Hydrochloric Acid.—Ten grams of C_6H_5SeOOH was dissolved in 120 cc. of water to make an approximately saturated

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(8) Pyman, *J. Chem. Soc.*, 116, 166 (1919)

solution at 0°, cooled in an ice-bath and saturated with hydrogen chloride gas. Toward the end of the reaction a solid came out, which was rapidly filtered on a Buchner funnel, using a mat made of the solid instead of filter paper, and refiltering the solid that went through while the mat was being prepared. Decomposition was checked by cooling all the filtering apparatus in ice water before using. The product was washed with cold concd. hydrochloric acid and dried in a desiccator over sulfuric acid. The yield was 23 g. or upwards of 200%, but the solid was later found to be full of water saturated with hydrochloric acid, which could not be removed by further drying. From the results of a rough chlorine analysis made on this wet substance, the yield was calculated to be approximately 80% of the theoretical. Five grams was dissolved in hot benzene and separated from the water by decanting through a filter wet with benzene, then saturated with hydrogen chloride and cooled, filtered and dried; m. p. 134°; mixed m. p. with sample described above, 133–134°, both with decomposition.

Anal. Calcd. for $C_6H_5SeCl_3$: Cl, 40.57. Found: Cl, 39.44.

(d) From Phenyl Ethyl Selenium Dichloride.—Twenty-three grams of phenyl ethyl selenide was converted in a flask to $(C_6H_5)(C_2H_5)SeCl_2$[5] and the ether and excess chlorine removed by pumping. The flask was heated to 80° in a Wood's metal bath. Effervescence occurred and the escaping gas was collected over water, at 25° and 760 mm. When effervescence had ceased, 2050 cc. of gas had been collected. The gas had the characteristic odor of ethyl chloride and gave a white precipitate with alcoholic silver nitrate. This volume of gas corresponds to about 6.5 g. of ethyl chloride or 81.4% of the calculated quantity, based on 23 g. of phenyl ethyl selenide. A yellow oil remained in the flask, which was, or contained, presumably, C_6H_5SeCl, but no attempt was made to isolate this compound, because of the belief that it might be unstable and the supply of material was limited. It was dissolved in 100 cc. of dry ether and saturated cold with chlorine. A yellowish, granular solid came out which was filtered off and recrystallized as described above; m. p. 133–134° (dec.); mixed m. p. with sample described above, 133–134" (dec.).

III. Treatment of Trihalides with Sodium Hydroxide

(1) **$C_6H_5SeBr_3$.**—Eight grams of $C_6H_5SeBr_3$ was added to a solution of 3.4 g. (3 moles) of sodium hydroxide dissolved in 25 cc. of water. Much heat was developed. The solution was filtered free from a trace of oily material and allowed to cool. A white crystalline solid came out which was filtered off and dried; m. p. 121–122° (m. p. C_6H_5SeOOH, 122–124"); yield, 3.5 g. or 87% of the theoretical. No C_6H_5SeOOH was at this time available, so part of the solid was dissolved in concd. nitric acid and warmed on the steam-bath until it was colorless. On cooling and seeding with a crystal of $C_6H_5SeOOH \cdot HNO_3$, prepared by the oxidation of diphenyl diselenide with nitric acid, the whole set to a white crystalline mass. It was filtered off, washed with cold water and dried in a desiccator; m. p. 110–112°; mixed m. p. with $C_6H_5SeOOH \cdot HNO_3$, 110–112°.

(2) **$C_6H_5SeCl_3$.**—Eight and a half grams of the trichloride was treated with 4 g. of sodium hydroxide exactly as described above: 8 g. or 79% of the theoretical was obtained; m. p. 121–122°; mixed m. p. with sample described above, 121–122".

The trihalides decompose when heated above their melting points, giving off hydrohalogen acid and leaving a dark oil which is uncrystallizable but reacts with cold water to give a very slightly soluble white crystalline solid, m. p. 162°, without decomposition. This compound is under investigation.

Summary

1. Phenyl selenium tribromide and phenyl selenium trichloride have been prepared by a variety of methods and their properties are described. Phenyl selenium triiodide could not be prepared.

2. The methods of preparation and reactions of these substances indicate that they are halogen salts of the hypothetical ortho benzene seleninic acid, $C_6H_5Se(OH)_3$, and that this latter compound has basic properties.

SWARTHMORE, PENNSYLVANIA
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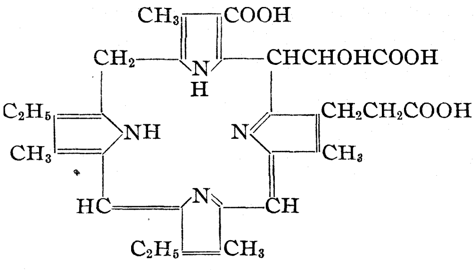
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Studies in the Chlorophyll Series. X. The Esters of Chlorin *e*

BY J. B. CONANT AND K. F. ARMSTRONG[1]

The structure of chlorin e has been established by a variety of transformations as dihydroisorhodoporphyrin glycolic acid (Formula I).[2]



I

When esterified with diazomethane, hydrochloric acid and methyl alcohol or by the action of dimethyl sulfate on the potassium salt, a trimethyl ester is formed. The identity of these esters has been investigated by converting them into the copper and zinc complex salts and taking mixed melting points. The results indicated that all the esters are identical. The complex metal salts of the esters of chlorin e are very suitable for the characterization of these compounds as they have sharp melting points; however, in our opinion all identification by mixed melting points in the chlorophyll series must be accepted with some reservation. Since this work was completed, a paper by Fischer and Siebel[3] has appeared in which the identity of these same esters was concluded from the mixed melting points of the esters themselves, and from their transformations with hydrogen iodide.

On hydrolysis with alkali, the trimethyl ester regenerates chlorin e. The saponification was carried out at room temperature and in an atmosphere of nitrogen to avoid the possibility of oxidation. The sole

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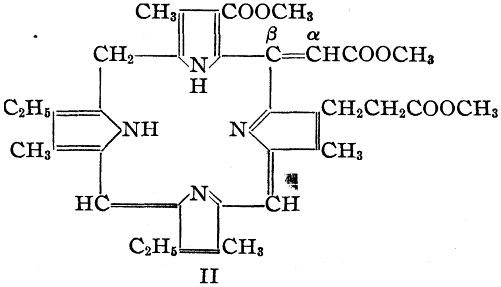
(1) Henry Fund Fellow at Harvard University.

(2) THIS JOURNAL, 55, 795 (1933).

(3) Fischer and Siebel, *Ann.*, 499, 84 (1932).

product was a crystalline chlorin e which on oxidation with molybdicyanide gave an almost quantitative yield of carbon dioxide; the other product of the reaction was chlorin k. This reaction is characteristic of the grouping —CHOHCOOH as has been shown in a study of chlorin e prepared from phaeophorbide.[2] The analysis of this regenerated chlorin e corresponds closely to the empirical formula $C_{34}H_{36}N_4O_6$ while the material prepared from phaeophorbide usually has the composition $C_{34}H_{38}N_4O_7$. In spite of this difference in analysis we are convinced of the essential identity of the two materials because of their identical behavior in the rather specific reaction with molybdicyanide. This reaction excludes the possibility that in the esterification of chlorin *e* the secondary alcohol group has been reduced to a CH2 group as at one time postulated by Fischer[4] in order to account for the analyses of the trimethyl ester and the regenerated chlorin e. As will be shown in the course of this paper, the behavior of chlorin e and its esters indicates that the characteristic grouping of these compounds is >CHCHOHCOOH(R) which in most instances is in equilibrium with >C=CHCOOH(R). Whether the hydrated or unhydrated form will be obtained as the isolated material may be expected to depend on slight variations of procedure. There is also the possibility that stereochemical modifications of chlorin e exist, both of which in solution are hydrated but one of which can be isolated in the solid state only as the unsaturated compound (dehydrated).

The most probable formula for the trimethyl ester is that of an unsaturated ester (11),a possibility previously suggested in a paper from this Laboratory.[5]



II

In his most recent paper Fischer[3] has also considered the possibility of the trimethyl ester being an unsaturated ester. He has pointed out that the addition of water to such a system might proceed so that the hydroxyl group is attached to the α carbon, instead of to the β carbon (formula II) as would normally be expected. The presence of two pyrrole nuclei might direct the addition in this manner.

To obtain further evidence in regard to the structure of the trimethyl

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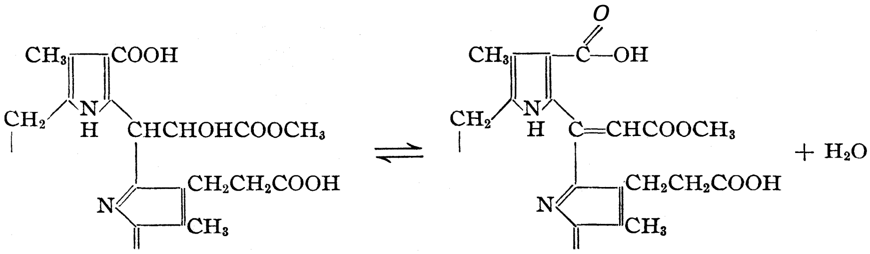
(4) Fischer, Moldenhauer and Süs, Ann., 486, 126 (1931).

(5) Catherine C. Steel, This journal, 53, 3174 (1931).

ester of chlorin e we have prepared two different monomethyl esters One of these (the beta ester) is formed by the partial methylation of chlorin e with diazomethane; the other (the alpha ester), by the partial hydrolysis of the trimethyl ester. On treatment with diazomethane in excess they are both converted into the trimethyl ester (identity established by mixed melting points of the copper derivatives) On ethylation with diazoethane they yielded two different diethyl methyl esters each having a copper derivative with a characteristic melting point. On further hydrolysis, the alpha ester (obtained by hydrolysis from the trimethyl ester) yields chlorin e.

By controlled hydrolysis of the trimethyl ester in cold 12% hydrochloric acid we have obtained a dimethyl ester, which appears to be different from the dimethyl ester obtained by Fischer and Siebel[3] by partial methylation with methyl alcohol and hydrochloric acid.

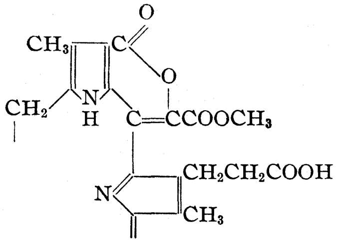
The structure of the alpha ester is established by the following facts. It is oxidized by molybdicyanide but no carbon dioxide is evolved; the product of oxidation (a new chlorin) on treatment with diazomethane yields only a diester. On pyrolysis the alpha ester readily loses only one mole of carbon dioxide yielding a monomethyl ester (a chlorin) which on treatment with diazomethane is methylated to a diester. If one considered only these reactions one would write formula III for the essential grouping in the molecule; the analytical data show, however, that a molecule of water has been lost; the anhydro form **IV,** therefore, suggests itself as the most probable formula.



(Anhydro **form**)

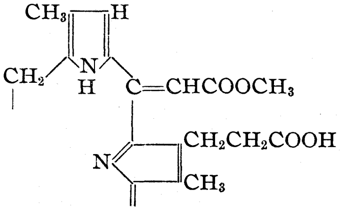
III IV

In solution the two forms would have to be interconvertible in order to explain the oxidation results; the mode of addition of a molecule of water was discussed in a preceding paragraph. Since the oxidation product of the alpha ester forms only a diester it must be analogous to chlorin *k*.[2] The keto group formed by the oxidation enolizes and the grouping $\rangle C{=}C(OH){-}COOCH_3$ on the bridge then loses water with the carboxyl group in the beta position. Formula V thus formulates the groups in this compound. The pyrolysis product of the alpha ester would have the grouping shown in VI. The analytical data correspond to these formulas.



V

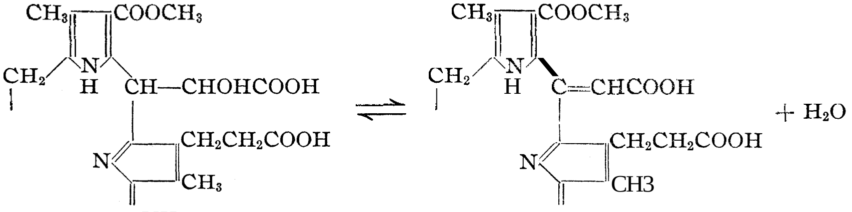
Monomethyl ester of chlorin k carboxylic acid
(oxidation product of alpha ester)



VI

Monomethyl ester of pyrochlorin e carboxylic acid
(Pyrolysis product of alpha ester)

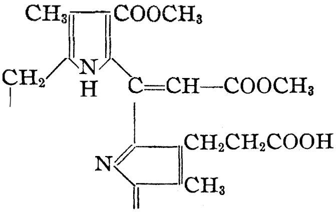
The structure of the beta ester is established by the fact that on oxidation with molybdicyanide, carbon dioxide is evolved. Unfortunately, the product which should be an aldehyde could not be isolated as it seemed to form an insoluble complex with the reagent. Experiments designed to obtain this interesting compound by the use of other oxidizing agents are in progress. On pyrolysis the beta ester loses carbon dioxide and yields a mixture of compounds from which an unidentified monomethyl ester of a porphyrin and a monomethyl ester of chloroporphyrin e_4 both of which were alkali soluble, were obtained. The fact that an ester of the latter porphyrin which contains a carboxyl group directly attached to the pyrrole ring was obtained after a drastic pyrolysis shows that the beta carboxyl group must have been esterified. This fact together with the oxidation results conclusively places the methyl group on the carboxyl group directly attached to the pyrrole ring. Like the alpha ester, however, the analyses of the beta ester indicate that the solid is an anhydro compound. In solution we must imagine that there is an interconversion of forms VII and VIII.



VII VIII

The positions of the methoxyl groups in the two isomeric monomethyl esters can be considered as well established; the nature of the anhydro linkage may be regarded as possibly less certain.

The structure of the dimethyl ester obtained by acid hydrolysis is established by these facts: its analysis corresponds to $C_{36}H_{40}O_6N_4$, it is not oxidized by molybdicyanide, and does not yield carbon dioxide



IX

on pyrolysis. It differs therefore from the trimethyl ester in that the propionic acid group is free (IX).

We have examined the behavior of the various esters of chlorin e in the "phase test." In addition to chlorin e triester, the diester and monomethyl ester made by its partial hydrolysis yield on shaking their ether solutions with 25% methyl alcoholic potassium hydroxide, unstable chlorins which on methylation at once yield phaeopurpurin 7, or on standing are converted into phaeopurpurin 18.

Chlorin *e* and beta monomethyl chlorin e do not yield phaeopurpurin. According to the ideas suggested in this Laboratory the essential reaction in an oxidative hydrolysis is the conversion of the group —CHOHCOOCH_3 (or its anhydro derivative) into —COCOOCH_3; this should be possible with the trimethyl, dimethyl and alpha monomethyl esters, but in chlorin e and beta monomethyl chlorin e the group —CH(OH)COO— would not be readily oxidized by the action of oxygen, or, if oxidized, would yield carbon dioxide.

The parallelism between the behavior of the ester of chlorin e which has the group $\rangle\text{C═CHCOOCH}_3$ and the phaeophorbides is very striking. In both cases the oxidative hydrolysis under the special phase test conditions is rapid and the products are identical. In the case of the alpha monomethyl ester the analogy is even closer, as the compound is oxidized by potassium molybdicyanide, thus behaving as though it had the grouping $\rangle\text{CHCHOHCOOCH}_3$ and yet its analyses correspond to the grouping $\rangle\text{C═CHCOOCH}_3$. As has been pointed out elsewhere,[6] the same situation exists in regard to the phaeophorbides; this parallelism seems to us to find a satisfactory explanation if the predominant form of phaeophorbide also contains the grouping $\rangle\text{CHCHOHCOOCH}_3$ in equilibrium with its anhydro form $\rangle\text{C═CHCOOCH}_3$.

We are indebted to Miss G. M. Ware and Mrs. S. E. Kamerling for the microanalyses reported in this paper.

Experimental

Chlorin e Trimethyl Ester.—Chlorin *e* was esterified with methyl alcohol as follows: 500 mg. of chlorin *e* was dissolved in 100 g. of methyl alcohol saturated with 30 g. of dry hydrogen chloride. After standing for forty hours at room temperature over half the product was alkali-insoluble trimethyl ester; yield, 200 mg. crystallized from ether. The alkali-soluble material was extracted with 6% hydrochloric acid and crystallized from ether; its analysis was: OCH_3, 8.12, 7.86; calcd. for two groups: 9.9.

Melting Points of the Trimethyl Esters of Chlorin e.—Samples of the trimethyl ester prepared by esterification with diazomethane, dimethyl sulfate and alkali and methyl alcohol and hydrogen chloride, respectively, were investigated by taking mixed melting points. All melting points recorded in this paper were taken with a block, with the same thermometer, and are uncorrected.

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(6) THIS JOURNAL, **55**, 839 (1933).

Ester, mode of preparation	M. p., °C.
(1) Diazomethane	209–210
(2) Dimethyl sulfate	209–210
(3) Methyl alcohol	213.5–214.5

Mixed melting points: (1) + (2), 209–210°; (1) + (3), 211.5–213.5°; (2) + (3), 210–211.5°.

A sample of the dimethyl sulfate ester, very slowly crystallized, melted at 213.5–214.5°. The diazomethane ester m. p. 209–210° did not have its melting point raised on recrystallizing from chloroform–methyl alcohol, nor lowered again on subsequent crystallization from ether. The melting point of the trimethyl ester is dependent on the rate of heating. Thus, samples placed on the block at temperatures up to 185° melt at the normal temperature; placed on the block at above 185° they melt at once, resolidify, and melt again at the normal temperature. A sample placed on the block at 205° melts but does not resolidify. It appears that a form melting at about 187° is transformed into the higher melting modification on melting, or slowly, on heating below its melting point.

Copper Derivative of Chlorin e Trimethyl Ester.—The method of Treibs and Wiedemann was followed.[7] To 100 mg. of ester in 3 cc. of chloroform, a solution of 30 mg. of copper acetate in 3 cc. of methyl alcohol was added, and the solution evaporated to dryness. The product was three times crystallized from acetone–petroleum ether (58–70°), forming slender dark green needles.

Spectrum in ether (1 mg. in 30 cc.; 5-cm. tube): I, 660.9–615.5; II, 591.8–581.5; III, 505.4–495.6. E.A. 434.2. Order, I, III, II.

Anal. Calcd for $C_{37}H_{40}N_4O_6Cu$: C, 63.44; H, 5.76; N, 8.00; Cu, 9.08; OCH_3, 13.30. Found: C, 62.33, 62.12; H, 5.90, 5.70; N, 7.91, 8.10; Cu, 9.56, 8.84; OCH_3, 14.44, 14.64.

The ether solution is blue green and does not fluoresce. The complex is extremely slowly decomposed by concentrated hydrochloric acid when in ether solution. Dissolved in equal parts of acetic acid and hydrochloric acid, it regenerates a chlorin in which the main red band is displaced further to the blue region than in chlorin *e*.

The copper derivatives of the trimethyl ester prepared in the three different ways were made separately and compared. Their spectra in ether were identical.

Esters, mode of preparation	M. p., copper derivatives, °C.
(1) Diazomethane	217–219
(2) Dimethyl sulfate	218–220
(3) Methyl alcohol	218–220

Mixed melting points: (1) + (2), 217–219°; (2) + (3), 218–220°; (1) + (3), 218–220°.

Zinc Derivative of **Chlorin *e* Trimethyl** Ester.—This was prepared exactly as the copper derivative, using zinc acetate: dark green needles; ether solution blue with strong red fluorescence.

Spectrum in ether (1 mg in 30 cc.; 5-cm. tube): I, 658.5–622.2; II, 605.9–585.7; III, 525.6–513.4; E.A. 440.5. Order, I, II, III.

Anal. Calcd. for $C_{37}H_{40}N_4O_6Zn$: C, 63.26; H, 5.74; N, 7.98; Zn, 9.31; OCH_3, 13.26. Found: C, 63.18, 63.24; H, 6.16, 5.84; N, 7.63, 7.84; Zn, 9.06, 8.87; OCH_3, 14.19, 14.04.

The chlorin regenerated on shaking the ether solution for a few minutes with 15% hydrochloric acid is identical in spectrum, color, and acid number with chlorin e trimethyl ester.

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[7] Treibs and Wiedemann, Ann., 471, 171 (1929).

The zinc derivatives of the three differently prepared chlorin *e* trimethyl esters have the same spectrum.

Esters, mode of preparation	M. p. Zn derivative, °C.
(1) Diazomethane	237–238
(2) Dimethyl sulfate	243–245
(3) Methyl alcohol	236–237

Mixed melting points: (1) and (2), 239–243°; (2) and (3), 236–243°; (1) and (3), 236–237". Repeated recrystallization did not raise the melting points of the diazomethane and methyl alcohol esters' zinc derivatives to that of the dimethyl sulfate ester It may be observed that our unsaturated formula for the triester gives a possibility for geometrical isomerism.

Copper Derivative of Chlorin *e* Triethyl Ester.—This was prepared by adding copper acetate in boiling methanol to the ester in chloroform. The triethyl ester was prepared by the use of diazoethane and agreed in its properties with those reported by Fischer and Siebel.[3] After two minutes of boiling, methanol and excess copper acetate were washed out with water, the chloroform solution dried and evaporated to dryness and the copper derivative crystallized from ether–petroleum ether. This procedure was used in all triethyl and mixed ethyl–methyl esters to avoid ester interchange in crystallizing from methanol; m. p. 154-155" Spectrum in ether (1 mg. in 30 cc.; 5-cm. tube): I, 655.4–617.4; II, 594.0–582.2; III, 506.6–494.4. E. A. 429.7. Order: I, III, II.

Anal. Calcd. for $C_{40}H_{46}N_4O_6Cu$: C, 64.70; H, 6.25; N, 7.55; Cu, 8.57; OC_2H_5, 18.22. Found: C, 64.49; H, 6.53; N, 8.95; Cu, 8.49; OCH_3, 18.72.

Regeneration of Chlorin *e* from the Trimethyl Ester.—700 mg. of crystalline trimethyl ester in 20 cc. pyridine was hydrolyzed with 7.5 g. potassium hydroxide dissolved in 100 cc. methyl alcohol and 5 cc. of water on standing overnight in a nitrogen atmosphere at room temperature. Almost the whole product was of acid number 3, and agreed in color, spectrum and acid number with chlorin e; yield 350 mg. of crystalline material (from ether). Dried for analysis in *vacuo* at 60°. Calcd. for $C_{34}H_{36}O_4N_6$: C, 68.42; H, 6.08; N, 9.39. Found: C, 69.21, 69.08; H, 6.37, 6.17; N, 9.39, 9.51; OCH_3, 0.0.

One hundred mg. of this chlorin was oxidized in a filtered oxidizing mixture made up as follows: 3 g. of potassium molybdocyanide, 2 cc. of acetic acid, 7 cc. of water, oxidized with permanganate and made up to 100 cc. with 10 cc. of pyridine and a molar solution of pyridine in acetone. An 80% yield of carbon dioxide (determined as barium carbonate) was obtained, together with chlorin k, identified by color and spectrum in ether and acid, and acid number. A duplicate experiment, conducted on the material which had been dried for analysis, gave 53% of carbon dioxide yield together with chlorin k and a small amount of unidentified porphyrin (acid number eight).

Experiments on the regeneration of chlorin *e* from its trimethyl ester at higher temperatures were unsatisfactory; 400 mg. of ester in 2 cc. of pyridine was given a hot quick saponification for four minutes with 30 cc. of boiling 25% potassium hydroxide in methyl alcohol in a nitrogen atmosphere. Fractionation of the product gave 160 mg. of crystalline chlorin extracted by 4% acid; found: OCH_3, 0.7%. Oxidation with molybdicyanide gave a yield of carbon dioxide of only 40%, even after correcting for the presence of a methoxy compound which would not yield carbon dioxide. Another experiment in which the solution was boiled for five minutes with 25% methyl alcoholic potash and for five more minutes after addition of an equal volume of water gave 175 mg. of chlorin; found: OCH_3, 0.95%. The corrected carbon dioxide yield was 54%. Since chlorin *e* and some of its derivatives give almost quantitative yields of carbon dioxide in oxidation with molybdicyanide, it is clear that in the above experiments, in addition to the methoxy derivative, and the chlorin which yields carbon dioxide and chlorin k, there is produced another chlorin which does not yield carbon dioxide on oxidation.

Alpha Monomethyl Ester of Chlorin *e*.—1.5 g. of chlorin e trimethyl ester dissolved in 10 cc. of pyridine was hydrolyzed with 300 cc. of 12% potassium hydroxide in methyl alcohol in a flask freed of oxygen and refilled with nitrogen. After standing for ten minutes at room temperature, the product was transferred to 2.5 liters of ether, washed free of pyridine and methyl alcohol, and acid fractionated. There was only a trace of unhydrolyzed trimethyl ester. The bulk of the material was a chlorin of acid number 5, identical in color and spectrum with chlorin *e*; yield of crystalline material from acetone–petroleum ether, 45%. There remained in the ether, alkali-soluble chlorin extractable with 7 or 8% hydrochloric acid.

Anal. (dried at 60° in *vacuo*). Calcd. for $C_{35}H_{40}O_7N_4$: C, 66.84; H, 6.42; N, 8.91; OCH_3, 4.94. $C_{35}H_{38}O_6N_4$: C, 68.81; H, 6.28; N, 9.18; OCH_3, 5.08. Found: C, 68.40, 68.66; H, 6.24, 6.51; N, 8.57, 8.56; OCH_3, 4.91, 5.35.

Five mg. was shaken in 10 cc. of ether with 1 cc. of 25% potassium hydroxide in propyl alcohol. Transferred to fresh ether after ten minutes, the product on fractionation was shown to consist of unchanged chlorin e alpha monomethyl ester and phaeopurpurin 18. The presence of unchanged material is explained by the separation of an insoluble potassium salt.

Conversion of Alpha Monomethyl Chlorin e to Trimethyl Ester of Chlorin *e*.—Sixty mg. of mono ester was introduced in 1 cc. of pyridine into 500 cc. of ether and methylated with diazomethane. The ether solution was successively washed with acid, alkali and water, dried and evaporated to dryness The residue was dissolved in 5 cc. of chloroform and treated with 20 mg. of copper acetate in 15 cc. of boiling methyl alcohol. On boiling off the chloroform the copper derivative crystallized in green needles Twice recrystallized from chloroform–methanol it melted at 217–219° (block uncorr.) and showed no depression with the copper derivative of the trimethyl ester made directly from chlorin e (m. p. 217–219°).

Oxidation of Alpha Monomethyl Chlorin *e*.—Electrometric titration of the oxidation with potassium molybdicyanide in acetone–pyridine showed that 79% of two equivalents of reagent were used in thirty-five minutes, and 102% in five hours; 60 mg. was oxidized in an apparatus designed to collect any carbon dioxide evolved, in a stream of nitrogen in a filtered oxidizing mixture made up as follows: 0.240 g. of molybdocyanide in 10 cc. of water, with I cc of glacial acetic acid, oxidized with permanganate and then made up with 8 cc. of pyridinc, and acetone to 90 cc. No carbon dioxide was evolved, whereas in a control experiment 58 mg. of chlorin e gave a 74% yield of carbon dioxide as barium carbonate. The product of the oxidation was a chlorin.

Monomethyl Ester of Chlorin k Carboxylic Acid

Chlorin from Oxidation of Alpha Monomethyl Chlorin *e*.—For preparative purposes 300 mg. was oxidized with a filtered mixture made as follows: 0.9 g. of potassium molybdocyanide, 20 cc. of water, 5 cc. of acetic acid oxidized with permanganate, and made up to 250 cc. with molar pyridine in acetone. After four hours the product was transferred to 2 liters of ether and washed free from acetone and pyridine; 7–12% acid extracted a small quantity of a mixture of chlorins which was discarded. The main product was a chlorin, extracted with 14 and 16% hydrochloric acid; yield 50% of the chlorin, crystallized from acetone–petroleum ether; OCH_3 calcd. for $C_{35}H_{36}O_6N_4$: 5.11. Found: 5.23, 5.34. The substance has a typical chlorin color in ether; the acid solution is blue with red fluorescence. A sample was methylated with diazomethane, and the product crystallized from acetone–petroleum ether, m. p. 260–262°. Acid number of ester, 16. Spectrum in ether (1 mg. in 30 cc. 5-cm. tube): I, 684.9–650.4; II, 616.7–603; III, 534.4–525.9; IV, 519.1–487.6. E.A. 432.2. Order: I, IV, III, II. Spectrum in acid: I, 674.8–635.8; II, 606.4–593.1; III, 570.0–557.4; IV, 5329–517.5. E. A. 4430. Order: I, IV, 111, II

Anal Calcd. for $C_{36}H_{38}N_4O_6$: C, 69.40; H, 6.16; N, 9.00; OCH_3, 9.97. Found: C, 69.23, 69.53; H, 6.91, 7.00; N, 8.29; OCH_3, 9.62, 9.18.

Monomethyl Ester of Pyrochlorin e Carboxylic Acid

Pyrolysis Product Alpha Monomethyl Chlorin e.—120 mg. was heated in 20 g. of diphenyl in an oil-bath at 215° for three and a half hours in a stream of nitrogen freed from oxygen by passing over red-hot copper wire, and dried with sulfuric acid and phosphorus pentoxide. The carbon dioxide evolved was absorbed in a potash bulb; yield of carbon dioxide 6 mg.; theory for 1 mole 8.65 mg.; 70% yield. The product was dissolved in 15% acid and washed with ether to remove diphenyl and then transferred to 1 liter of fresh ether; 4 and 5% acid extracted a little porphyrin; 6 and 7% acid removed traces of porphyrin and some chlorin. The main product was a chlorin, extracted with 10 and 11% acid; yield 50 mg., crystallized from acetone–petroleumether, 42%.

Anal Calcd. for $C_{34}H_{38}O_4N_4$: C, 72 04; H, 6.76; N, 9.88; OCH_3, 5.47. Found: C, 72.20, 71.44; H, 7.15, 6.72; N, 9.76, 9.78; OCH_3, 5.81. Esterified with diazomethane it gave a diester; OCH_3: 10.02, 10.24, m. p. 206–208" (block uncorr.). Spectrum (1 mg. in 30 cc. ether, 5-cm. tube). Ether solution typical chlorin color. I, 682.4–647.6; II, 613.8–602.3; III, 531.6–525.0; IV, 507.6–485.3. E. A. 433.0. Order: I, IV, III, II.

Spectrum in acid. Acid solution greenish blue with red fluorescence. I, 677.2–631.8; 11,611.2–598.4; III, 532.6–521.8; E.A. 446.7 Order. I, III, II.

Diethyl Alpha Monomethyl Ester of Chlorin e.—The alpha monomethyl ester was treated with diazoethane; the product was fractionated and extracted with 11% acid, transferred to ether and crystallized; m. p. 152°.

Anal. Calcd. for $C_{39}H_{46}O_6N_4$: C, 70.22; H, 6.96; N, 8.40. Found: C, 70.15; H, 6.78; N, 8.09.

The copper derivative prepared in the usual manner and crystallized from ether–petroleum ether melted at 166.5–167° (block uncorr.).

Beta Monomethyl Ester of Chlorin *e*.—0.614 g. of dry chlorin e (0.001 mole) dissolved in 2 cc. of dry pyridine (distilled over potassium hydroxide) and 50 cc. of dry dioxane (freshly distilled from sodium) was treated with a dry ether solution containing 0.0012 mole of diazomethane (standardized with benzoic acid), in a three-necked flask fitted with mercury-sealed stirrer, a calcium chloride tube, and a tap funnel delivering below the surface of the liquid. The diazomethane was added during twenty minutes with stirring, and after standing overnight the mixture was transferred to 2.5 liters of ether and washed free of dioxane. Three extracts with 3% acid and one of 4% sufficed to remove unmethylated chlorin e. The main product was isolated with 5% acid.

Anal. 3% fraction 2.80% OCH_3; 4% fraction 4.89% OCH_3; 5% fraction 5.07% OCH_3.

The yield of 5% fraction, crystallized from acetone–petroleum ether, 250 mg.. ***was*** 40%. The acid number is 5, the color in ether and acid and the spectrum are identical with that of chlorin e.

Anal Calcd. for $C_{35}H_{40}O_7N_4$: C, 66.84; H, 6.42; N, 8.91; OCH_3, 4.94. $C_{35}H_{38}O_6N_4$: C, 68.81; H, 6.28; N, 9.18; OCH_3, 5.08. Found: C, 69.00, 68.72; H, 6.67, 6.32, N, 8.48, 8.83; OCH_3, 5.11, 5.05.

No conversion to phaeopurpurin under "phase test" conditions could be obtained

Unextracted with 5% acid in the products of the partial methylation of chlorin *e*, is an alkali-soluble chlorin of acid number 7. Its yield can be increased by employing 2 moles of diazomethane. The analysis indicates it to be impure dimethyl ester. Calcd. OCH_3, 9.9. Found: 8.3, 8.7.

Oxidation of Beta-Monomethyl Ester of Chlorin *e*.—A 5-mg sample used up 101% of 2 equivalents of potassium molybdicyanide in acetone–pyridine solution in sixty minutes; 62 mg. was oxidized with a filtered oxidizing mixture containing 0.4 g. of molybdocyanide, 2 cc. of glacial acetic acid, and 12 cc. of water, oxidized with permanganate and made up with 8 cc. of pyridine and acetone to 90 cc. The carbon dioxide evolved was swept out with nitrogen and weighed as barium carbonate: yield of barium carbonate in four hours, 13.4 mg.; calcd. for 1 mole 19.5 mg. or 69% yield. In a duplicate experiment 125 mg. gave 36.7 mg. of barium carbonate; calcd., 36.8; 100% yield.

On pouring into ether preparatory to working up the product, the whole material separated as an insoluble scum, which dissolved in 1% hydrochloric acid to give a blue, strongly fluorescing solution, which again gave the scum on neutralization. The scum was also soluble in alkalies. It appeared that the oxidation product had formed an insoluble complex with the oxidizing agent. The complex was not broken by hydrogen sulfide in acid, alkaline or ammoniacal solution, nor by continuous ether extraction of the acid solution. Other experiments designed to break down the complex without demethylating the chlorin proved unsuccessful.

Pyrolysis of Beta-Monomethyl Ester of Chlorin *e*.—120 mg. of ester was heated in 20 g. of diphenyl in a bath maintained at 245–265° in an oxygen-free, dry nitrogen stream for three hours. Carbon dioxide equivalent to 0.86 mole was evolved. The product was dissolved in acid, washed free of diphenyl with ether, transferred to fresh ether and the mixture of alkali soluble porphyrins obtained, acid fractionated. The products were a porphyrin extracted with 2% acid, identified by its color in ether and acid, and by its spectrum as chloroporphyrin e_4 (monoester).

Anal. OCH_3, calcd., 5.48. Found: 6.09.

Another porphyrin was extracted with 7% acid, but was not identified; OCH_3 found, 5.09.

Conversion of Beta-Monomethyl Ester to Normal Chlorin e Trimethyl Ester.—A sample was methylated with excess diazomethane, fractionated and transferred to fresh ether and converted into the copper derivative as described above. It melted at 217–219" (block uncorr.) and the mixed melting point with the copper derivatives of chlorin *e* trimethyl ester made directly from chlorin e, and the trimethyl ester made from alpha monomethyl chlorin e showed no depression.

Diethyl Beta-Monomethyl Ester of Chlorin e.—A sample of the beta ester treated with diazomethane gave on fractionation a triester, crystallized from ether, m. p. 155–157'. The copper derivative prepared in the usual way, crystallized from ether–petroleum ether, m. p. 187–189°.

Chlorin e Dimethyl Ester, by the Acid Hydrolysis of the Trimethyl Ester.—Suitable conditions were found by following the hydrolysis of the trimethyl ester in 12% hydrochloric acid, determining the percentage of alkali solubility and the methoxyl content of the alkali soluble material with time. At room temperature the dimethyl ester first formed is later slowly hydrolyzed to give a monomethyl ester. For preparative purposes, 750 mg. of triester was dissolved in 250 cc. of 12% hydrochloric acid, and stood at room temperature for three hours. On working up the product, about 100 mg. of triester remained unhydrolyzed. The alkali-soluble material, crystallized from ether, gave 310 mg. of excellent crystals, of no definite melting point, sintering on the block above 230°. The spectrum and color is identical with that of chlorin e.

Anal. Calcd. for $C_{36}H_{40}O_6N_4$: C, 69.19; H, 6.45; N, 8.97; OCH_3, 9.93. Found: C, 69.40, 69.61; H, 6.52, 5.90; N, 9.07, 8.83; OCH_3, 9.72, 9.31.

The dimethyl ester is not oxidized by molybdicyanide; 5 mg. of dimethyl ester in 15 cc. of ether, shaken with 1.5 cc. of 25% potassium hydroxide in methyl alcohol, gave unstable chlorins which on methylation at once gave dimethyl phaeopurpurin 7, or on standing, phaeopurpurin 18.

Pyrolysis of Dimethyl Ester.—100 mg. of material was heated in diphenyl with a bath temperature of 250–270° in an oxygen-free, dry nitrogen stream. The carbon dioxide slowly evolved (none in the first hour) corresponded to 0.35 mole. By comparison, both alpha and beta monomethyl esters lose the bulk of their carbon dioxide in the first hour. The product consists of a mixture of unidentified alkali-soluble porphyrins.

Summary

1. The trimethyl ester of chlorin *e* has been prepared by a number of methods and the identity of the products established through the melting points of their metallic derivatives.

2. On hydrolysis, the trimethyl ester regenerates a chlorin e in which the glycolic acid side chain has been shown to be present.

3. Two isomeric monomethyl esters and one dimethyl ester have been prepared and their structures established by their transformations. Two isomeric diethyl methyl esters have been prepared.

4. The bearing of these results on the structure of phaeophorbide *a* has been discussed.

CAMBRIDGE, MASSACHUSETTS

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Studies in the Chlorophyll Series. XI. The Position of the Methoxyl Group

BY JAMES B. CONANT AND EMMA M. DIETZ

In the fifth paper of this series we proposed a formula for chlorophyll *a*,[1] in which a carbomethoxy group was placed in the beta position of one of the pyrrole rings. This seemed necessary as the facts in regard to oxidative hydrolysis (phase test) given in the third and fourth papers[2] showed that a methoxyl group survived this degradation and was present in phaeopurpurin 7. This compound on pyrolysis yielded a monomethyl chlorin f and thus was shown to contain a carbomethoxy group attached to one of the pyrrole nuclei. The yield of phaeopurpurin 7 (a monomethyl ester) was always very low, however, and all attempts to increase the yield by changing the conditions of oxidative hydrolysis failed. The chief product was always the unstable chlorin which on standing yields phaeopurpurin 18. In this connection we may mention that we have not been able to observe the conversion of phaeopurpurin 7 to phaeopurpurin 18 on standing in solution as reported by Fischer.[3]

The small yield of phaeopurpurin 7 led us to suspect that it might arise from some impurity in our phaeophorbides, and this has proved to be the case. We have been able to obtain a sample of methyl phaeophorbide a

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[1] THIS JOURNAL, **53**, 2382 (1931).
[2] *Ibid.*, **52**, 3013 (1930); **53**, 359 (1931).
[3] Fischer, *Ann.*, **498**, 196 (1932).

which after several recrystallizations yielded no phaeopurpurin 7 on oxidative hydrolysis. It is difficult, however, to remove the precursor of phaeopurpurin 7 from the phaeophorbides. Material prepared from the chlorophyllides yields small amounts of phaeopurpurin 7 unless carefully recrystallized. Crude methyl phaeophorbide *a* prepared from commercial phaeophytin by the usual Willstatter procedure is very rich in this impurity. It can be purified by a partial hydrolysis procedure described in detail in the experimental portion of this paper, which also removes other impurities. The methyl phaeophorbide *a* thus purified, crystallizes beautifully and we believe it to be as pure as the material prepared through the chlorophyllides.

The analyses of the pure methyl phaeophorbides (from phaeophytin or through the chlorophyllides) correspond closely to the formula $C_{36}H_{38}N_4O_5$ instead of $C_{36}H_{40}N_4O_6$ previously assigned. This fact has recently been emphasized by Stoll and by Fischer,[4] and led the latter to modify his formula for chlorophyll *a*. Stoll's formulas for chlorophyll *a* and chlorophyll b seem to us to be excluded by a great number of considerations, only one of which will be considered here. According to his formula the hydrolysis of phaeophorbide a to chlorin *e* is an oxidative reaction and he states that he is able to prevent chlorin formation by adding a reducing agent to the hydrolyzing mixture.[5] (He has as yet published no experimental details, however.) Mr. J. L. Hartwell[6] in this Laboratory has shown that the formation of chlorin *e* by hydrolysis of the phaeophorbides not only proceeds in a nitrogen atmosphere, but that as powerful a reducing agent as a sulfonated anthrahydroquinone may be present without affecting the result. It seems to us impossible that an oxidative reaction is involved in the formation of chlorin e from phaeophorbide *a*.

The parallelism between the behavior of the esters of chlorin e and the phaeophorbides has been pointed out in the preceding paper? The analysis of chlorin e and its esters corresponds to an oxygen content of O_6 while the reactions call for a formula with O_7; the phaeophorbides of the *a* series behave as if they contained six oxygen atoms but the analyses correspond to a content of five oxygen atoms. We believe that the most probable explanation is that in both cases one is dealing with an unsaturated compound which easily adds water in solution forming an hydroxy compound, the water being lost again on crystallizing and drying. If this is the case, at least *in solution,* the phaeophorbides like the chlorin e esters are hydroxy compounds.

The oxidative hydrolysis of pure phaeophorbide a in the presence of very dilute alkali resulted in the formation of a monomethyl ester of a chlorin of

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(4) Stoll *and* Wiedemann, *Naturwissenschaften,* 628, 706, 791 (1932); *Helv. Chim. Acta,* 16, 1128, 1280 (1932); Pischer, Ann., 499, 84 (1932).

(5) Stoll, *Helv. Chim. Acta,* 15, 1284 (1932).

(6) Unpublished results.

(7) Tars JOURNAL, 55, 829 (1933).

the "oxidized series." It is stable in solution but on treatment with diazomethane forms dimethyl phaeopurpurin 7 (a triester). A diethyl phaeopurpurin 7 (a diethyl methyl ester) was made by treating the chlorin with diazoethane. On heating this compound with pyridine and sodium carbonate according to Fischer's method,[8] a diethyl ester of isorhodoporphyrin was formed. This shows that the carbomethoxy group of the chlorin was part of the bridge grouping; the formation of a methoxyl-free isorhodoporphyrin on heating the chlorin itself also demonstrated the position of the OCH_3. These transformations thus serve to confirm the position of the methyl group in chlorophyll a assigned by Fischer[9] We propose to designate this new chlorin as the alpha monomethyl ester of chlorin g, since it contains the grouping $—COCOOCH_3$ on the bridge. As pointed out in the third paper of this series, the "unstable chlorins" are probably identical with Willstatter's phytochlorin g. It is interesting that when the bridge carboxyl group is esterified the chlorin passes into the phaeopurpurin structure only on treatment with diazomethane. On hydrolysis the ester is transformed into the unstable chlorin (chlorin g) which spontaneously passes into phaeopurpurin 18.

The precursor of phaeopurpurin 7 is a substance of considerable interest. It is clearly very similar to the phaeophorbides (or the chlorophyllides as the case may be) as it is difficult to purify these compounds from it. Since phaeopurpurin 7 can be transformed into dimethyl phaeopurpurin 7 by the action of diazomethane, and on pyrolysis yields chlorin f monomethyl ester, we are clearly dealing with a compound with the same nucleus and carbon skeleton as in the normal form of phaeophorbide a. The position of the methoxy group, however, is different. The phaeopurpurin 7 prepared from crude chlorophyll or phaeophytin appears to have the same structure as the phaeopurpurin 7 formed by hydrolysis of dimethyl phaeopurpurin 7. Both compounds yield monomethyl chlorin f, carbon monoxide and carbon dioxide on pyrolysis, and have very similar properties except for a slight difference in color, spectrum and acid number. The position of the methoxyl group in both substances is established by its survival in chlorin f monomethyl ester (pyrolysis) and its resistance to hydrolysis by dilute alkali; as will be shown in a later paper, an ester group involving the propionic acid is rapidly hydrolyzed by even dilute alkali. On vigorous hot alkaline hydrolysis, methoxyl-free chlorin f is formed. All these facts show that the grouping $—COOCH_3$ is on the pyrrole ring in phaeopurpurin 7.

The precursor of phaeopurpurin 7 occurs in relatively small quantities (1 to 3%) in the crude chlorophyll of a number of green plants which we have so far examined (spinach, Datura, and representatives of filamentous chlorophyceae and marine phaeophyceae) and in commercial phaeophytin. The largest amount (20%) was found in the mother liquors from crystalline

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(8) Fischer, Ann., 490, 87 (1931)

(9) Fischer, *ibid.*, 490, 42 (1932).

ethyl chlorophyllides prepared from Datura. The estimation of its presence is possible by carrying out a vigbrous oxidative hydrolysis ("phase test" conditions) of the crude chlorophyll or phaeophytin (preferably free from the carotenoids), allowing the solutions of the unstable chlorins to stand for three to five days and carefully fractionating with acid. The normal chlorophyll *a* component is thus transformed into phaeopurpurin 18 which is easily separated by its high acid number. The oxidized rhodins are also removed only by strong acid. If the oxidative stage of the hydrolysis is not rapid enough, small amounts of chlorin e and rhodin g may also be formed. The latter is difficult to separate from phaeopurpurin 7 but a procedure described in detail in the experimental section of this paper may be employed.

It seems to us that there can be no escape from the conclusion that there are two very similar forms of chlorophyll *a*. In the predominant form the carbomethoxy group is located on the bridge; in the other form it is located on the pyrrole ring. We are now engaged in an attempt to separate in a pure state this second form of chlorophyll *a* or its related chlorophyllide or phaeophorbide; we also intend to examine a greater variety of green plants for the relative distribution of the two forms. It appears probable that a similar situation exists in regard to chlorophyll b, and we are engaged in a similar line of investigation in regard to the location of the methoxyl group in this compound.

The formula for chlorophyll *a* which we suggested in the previous paper is impossible for the predominant form of chlorophyll *a* because of the position of the methoxyl group; it may represent the second form, however. Fischer's formula containing a carbocyclic ring is, of course, satisfactory as far as the position of the methyl group is concerned for the predominant form, but is not possible for a compound containing the potential carbomethoxy group on the pyrrole ring (as appears to be the case in the second form). We are still inclined to favor a formula for chlorophyll *a* that contains a secondary hydroxyl group attached to the bridge because of the dehydrogenation results considered in our previous papers; the analogy between the chlorin e esters and the phaeophorbides also influences us in this choice. We do not feel that the presence of a carbocyclic ring in chlorophyll a or the phaeophorbides is proved by the transformation of these substances into phaeoporphyrin a_5 and phylloerythrin which has been carried out by Fischer.[10] The possibility is not excluded that the carbocyclic ring which Fischer has shown to be present in phylloerythrin was closed in the reaction by which the chlorophyll compounds are transformed. Such a ring closure does in fact occur under only slightly more drastic conditions in the preparation of phylloerythrin from the chloroporphyrins.[11]

It would seem extremely probable that the structural formulas of the two

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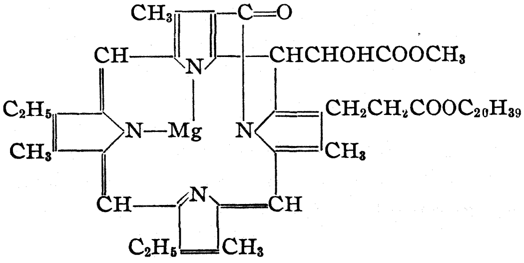
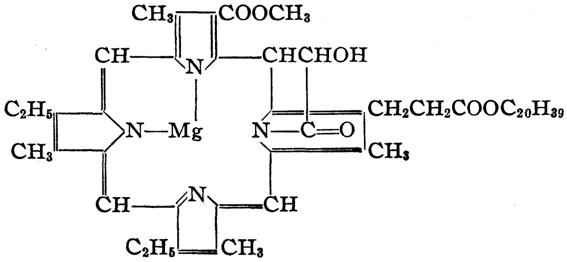
(10) Fischer, Ann., 486, 107 (1931).

(11) Fischer *and Moldenhauer, ibid., 481, 152* (1930).

forms of chlorophyll *a* are very similar if the compounds differ only slightly in their properties. A formula is therefore desirable which allows the interchange of the methoxyl group between the potential carboxyl groups of the bridge and pyrrole ring without serious structural modification. The lactam formula which we mentioned in the fifth paper[12] as an alternative to our anhydride formula satisfies these requirements. The formula for the predominant form of chlorophyll *a* (a_1) would then be as shown in I, and the other form (a_2)—the precursor of phaeopurpurin 7—would be represented as II.



I Chlorophyll a_1



II Chlorophyll a_2

We are indebted to Miss G. M. Ware and Mrs. S. E. Kamerling for the microanalyses reported in this paper.

Experimental

Purification of Methyl Phaeophorbide a.—The methyl phaeophorbide a obtained in the usual way from commercial phaeophytin gives unsatisfactory analyses even after several recrystallizations. On hot rapid saponification in nitrogen as much as 15% of chlorin f may be obtained along with the chlorin e, indicating the presence of an oxidized impurity in the methyl phaeophorbide. After a carefully controlled rapid treatment with dilute alkali, however, the methyl phaeophorbide which remains appears to be as pure as preparations from methyl chlorophyllide a. Its analysis shows a content of five oxygen atoms and on hot rapid saponification only a trace of high chlorin results. A typical purification experiment is as follows: three grams of methyl phaeophorbide a was dissolved in 150 cc. of pyridine and 750 cc. of acetone in a three-liter three-necked flask, fitted with a gas inlet tube for nitrogen, a mercury-sealed stirrer and a conical glass funnel of 750 cc. capacity. The neck of the funnel was closed by a one-holed rubber stopper at the end of a glass rod. This arrangement permitted the rapid addition

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(12) THIS JOURNAL, 53, 2384 (1931).

of large volumes of alkali or acid as needed. The solution was refluxed in nitrogen for ten minutes to remove oxygen, then cooled to 0° with nitrogen bubbling through. At the same time 750 cc. of 1% potassium hydroxide solution was similarly refluxed for ten minutes and cooled to 0° in nitrogen. Then the stopper carrying the nitrogen inlet tube was loosened and the alkali was rapidly added through the funnel to the violently stirred pyridine–acetone solution. The plunger was replaced in the funnel and after fifteen seconds, 11% hydrochloric acid was added in the same way, precipitating the material in fine amorphous form. This dissolved readily on shaking with five liters of ether and formed a violet-red solution. The alkali-soluble material was removed with 0.02 *N* potassium hydroxide solution. The residue was then extracted with portions of iced 11 to 14% acid until the extracted material had the same spectrum as the main solution, which was finally concentrated without further treatment. The yield in several experiments was 40 to 65%. The alkali-soluble by-products are mainly monomethyl chlorin *e*, and pheopurpurin 18 resulting from hydrolysis of impurities and from oxidative hydrolysis of good methyl phaeophorbide *a* due to unremoved traces of oxygen. The product separated in well-formed black crystals with a blue luster. The spectra in ether and acid are identical with those of methyl phaeophorbide a prepared from the chlorophyllides, and the yellow phase color is very marked on shaking the ether solution with methyl alcoholic potassium hydroxide.

Analyses of several samples of methyl and free phaeophorbides are listed below. Those from chlorophyllides were obtained by acid treatment and fractionation of crystalline ethyl or methyl chlorophyllide mixtures of the alpha and beta compounds, prepared from Datura according to the Willstatter procedure. The "regenerated" methyl phaeophorbide *a* was prepared by diazomethane treatment of phaeophorbide *a* from purified methyl phaeophorbide a.

Anal. Calcd. for $C_{36}H_{38}O_5N_4$: C, 71.30; H, 6.3; N, 9 24; OCH_3, 10.2.

	C	H	N	OCH_3
Methyl phaeophorbide a purified as above	71.15	6.6	9.01	10.61
	71.38	6.9		9.28
Methyl phaeophorbide a from methyl chlorophyllides	71.04	6.57	9.28	10.36
	71.27	6.75	9.38	10.68
	71.44	7.03		
Methyl phaeophorbide a regenerated	71.44	6.55	9.05	9.3
	71.07	6.55	8.95	10.0
	70.84	6.35		
Methylated phaeophorbide *a* from ethyl chlorophyllides	71.18	6.45	9.56	
	71.12	6.45	9.31	

Calcd. for $C_{35}H_{36}O_5N_4$: C, 70.95; H, 6.1; N, 9.46; OCH_3, 5.3
Calcd. for $C_{35}H_{38}O_6N_4$: C, 67.72; H, 6.25; N, 9.66; OCH_3, 5.35

Phaeophorbide a from purified methyl phaeophorbide a dried at 10^{-3} mm. press.	69.78	6.26	9.28	4.7
	69.70	6.63	9.10	5.1
Phaeophorbide *a* from ethyl chlorophyllides	70.3	6.35	9.50	

Rate of Hydrolysis of Methyl Phaeophorbide a.—Preliminary experiments were carried out on the hydrolysis of methyl phaeophorbide *a* at 0° in an aqueous butyl carbitol–pyridine mixture 0.04 N in potassium hydroxide and in a nitrogen atmosphere. The results indicate that there is a rapid conversion to monomethyl chlorin *e* with loss of one methoxyl group and apparently without the intermediate formation of phaeophorbide **a.** The rate of formation of monomethyl chlorin e was as follows: 40% in five minutes, 55% in ten minutes, and 80% in forty-five minutes. The concentration of phaeophorbide a was never greater than 5%. The second methoxyl group is lost with much greater difficulty. After thirty-six hours under the same conditions only one-fourth of the product was free chlorin *e*. Phaeophorbide *a* in aqueous pyridine at 0° in nitrogen and with an alkali concentration of 0.45 mol., also changes rapidly to monomethyl chlorin e. The analysis of the product corresponds to a quarter of a methoxyl group even after twenty-four hours.

The hydrolysis of phaeophorbide *a* proceeds very rapidly in the presence of oxygen, forming monomethyl chlorin *g* which is then transformed more slowly with loss of methoxyl content to phaeopurpurin 18. The rate of formation of "unstable chlorins" including the monomethyl ester of chlorin *g* in a phaeophorbide *a* solution 0.02 molar in alkali was as follows: 40% in two minutes, 80% in ten minutes.

Monomethyl Ester of **Chlorin** g.—This substance was prepared by mild oxidative hydrolysis of phaeophorbide a obtained from its methyl ester purified as above, or from methyl chlorophyllide a. A solution of 450 mg. of phaeophorbide *a* in 125 cc. of pyridine and 250 cc. of water was cooled to 0° in an ice-bath and stirred by a stream of oxygen for thirty minutes. Then 75 cc. of 0.06 N aqueous potassium hydroxide was added. making the total alkalinity 0.01 *N*, and the gas stream was continued for thirty minutes The product was transferred to three liters of ether and allowed to stand overnight to enable any unstable chlorins present to change over to phaeopurpurin 18. Extraction with 6 to 8% acid removed some low chlorin, 12 to 14% acid removed the main product, and the residue contained small amounts of unchanged phaeophorbide and of phaeopurpurin 18 resulting from demethylation of the desired chlorin. A convenient test for the homogeneity of the last extracts of monomethyl chlorin g is treatment with diazomethane which changes the spectrum completely and instantly to that of phaeopurpurin 7. The yield of chlorin was 30 to 60% in several experiments.

A sample was recrystallized for analysis from acetone–ligroin, forming small black crystals. The color in ether is bright green with a red fluorescence; in acid, green. The acid number is 12.

The spectrum in ether (a solution of one milligram in 30 cc. measured in a 55-mm. tube): I, 687—646; II, ---620—600---; III, ---566---554--- (very hazy); IV, 533—520; V, 509—481. E. A.: 438. Order: I, IV, V, II, III.

The spectrum in 16% hydrochloric acid: I, 589—569; II, ---541---521--- (very faint). E. A.: 456. Order: I, II.

Anal. Calcd. for $C_{35}H_{38}O_7N_4$: C, 67.08; H, 6.1; N, 8.95; OCH_3, 4.95. Found: C, 66.66, 66.90; H, 5.9, 6.0; N, 8.95, 9.19; OCH_3, 4.6, 4.4.

When monomethyl chlorin g is shaken in ether solution with 25% potassium hydroxide in propyl alcohol, an unstable chlorin is obtained which changes to phaeopurpurin 18 slowly on standing, or immediately on warming.

Pyrolysis of Monomethyl Chlorin g.—Pyrolysis in diphenyl results in the removal of the two bridge carbon atoms and methyl group forming free isorhodoporphyrin as the main product. A solution of 300 mg. of the chlorin in 50 g. of diphenyl was boiled in nitrogen for five minutes. The product in 6 liters of ether had a brown-red color and was worked up in the usual manner. The main product, a porphyrin, was extracted with 8 to 10% acid, leaving traces of chlorin in the mother liquor. The spectra in acid and ether were identical with those of isorhodoporphyrin; yield, 50 mg. of crystalline isorhodoporphyrin.

Anal. Calcd. for $C_{33}H_{38}N_4O_4$ (monomethyl ester): OCH_3, 5.60. Found: OCH_3, 0.61, 0.84.

Transformation to **Dimethyl Phaeopurpurin 7.**—Monomethyl chlorin g unlike the ordinary "unstable chlorins" is unchanged after standing for a few weeks in ether solution, but on treatment with diazomethane, dimethyl phaeopurpurin 7 (a triester) forms immediately. This product was identified by spectrum in acid and ether, by acid number and by analysis. It was thus shown to be identical with "synthetic" dimethyl phaeopurpurin 7.

The spectrum in ether: I, 712—651; II, ---638—613--- (very weak); III, 554---549—529---; IV, 516---512489---. E. A. 443. Order: I, IV, III, II.

Anal. Calcd. for $C_{37}H_{42}O_7N_4$: C, 67.9; H, 6.4; N, 8.56; OCH_3, 14.2. Found: C, 67.75; H, 6.53; OCH_3, 14.0, 13.7.

Conversion of Diethyl Methyl Ester to Diethyl Isorhodoporphyrin.—The carefully fractionated ether solution of a preparation of monomethyl chlorin g was treated with diazoethane whereby diethyl phaeopurpurin 7 (phaeopurpurin 7 is a monomethyl ester) was formed. The isolated crystalline product (430 mg.) was dissolved in 75 cc. of pyridine, 1.5 g of anhydrous sodium carbonate was added and the solution was refluxed for three hours. On transferring to 10 liters of ether the solution had a good porphyrin color, the main product being diethyl isorhodoporphyrin with traces of a low porphyrin and of a high chlorin. The yield was 135 mg. After recrystallization from chloroform–methyl alcohol, the melting point was 240–241°. The recrystallized diethyl ester prepared by the action of diazoethane on the ferricyanide oxidation product of chlorin *f* melted at 236–238°.[13] The mixed melting point lay between these two values.

Anal. Calcd. for $C_{36}H_{44}O_4N_4$ (diethyl ester): C, 71.52; H, 7.6; N, 9.7; OC_2H_5, 15.3. Found: C, 71.90, 71.71; H, 6.91, 6.48; N, 9.30; OC_2H_5, 15.4, 14.0.

A further identification of the product as a diethyl ester was obtained by using a solution of trimethylamine as absorbent in the Zeisel determination.[14] Authentic samples of methyl ethyl and of diethyl isorhodoporphyrin were analyzed at the same time to serve as controls on the method.

Preparation of Phaeopurpurin 7 from Various Plant Sources

(a) From Commercial Phaeophytin.—Oxidative hydrolysis under phase test conditions of phaeophytin results in the formation of unstable chlorins which change over in the course of several days to phaeopurpurin 18 and 1 to 2% of phaeopurpurin 7. The evidence indicates that the major form of chlorophyll *a* has a carbomethoxy group on a carbon atom attached to the bridge position as in alpha monomethyl chlorin *g*, which probably precedes phaeopurpurin 18 in the above-mentioned hydrolysis of phaeophytin. The preparation of phaeopurpurin 7 in this way was carried out as follows. Eighteen grams of phaeophytin was dissolved in 60 cc. of pyridine, the solution was diluted with 4 liters of ether and then shaken for eight minutes with a solution of 400 cc. of 20% potassium hydroxide in propyl alcohol which had been previously saturated with oxygen. The product was transferred to ten liters of ether and a large amount of ether-insoluble scum was formed. After standing for five days the solution was fractionated. Some strongly basic chlorin was removed by 4 to 7% hydrochloric acid and the phaeopurpurin 7 was then extracted with 8 to 13% acid. The yield after refractionation was 230 mg. of very small black crystals Phaeopurpurin 18 was isolated from the residue in 15% yield.

Anal. Calcd. for $C_{35}H_{38}O_7N_4$: OCH_3, 4.95. Found: OCH_3, 3.97, 4.14

(b) From Spinach Chlorophyll.—An oxidative hydrolysis was carried out under similar conditions on chlorophyll isolated from spinach according to the Willstatter procedure. A solution of 25 g. of chlorophyll in 70 cc. of pyridine was added to 4.5 liters of ether and the whole shaken for eight minutes with 450 cc. of 20% potassium hydroxide in propyl alcohol. (The alkali was previously saturated with oxygen) The green mixture was diluted and the product transferred to 12 liters of ether. After four days the solution was fractionated. Extraction with 6% acid removed some low

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(13) THIS JOURNAL, 55, 795 (1933).

(14) Pregl, "Microanalysis," second English edition, p. 190.

chlorin. Extraction with 8 to 13% acid removed a mixture of phaeopurpurin 7 and rhodin g which it was impossible to resolve by further fractionation. A separation was easily accomplished, however, by making use of the rapid reaction of the rhodin g with semicarbazide hydrochloride to form a derivative of low acid number. This could then be readily removed from the unchanged phaeopurpurin 7 by acid fractionation. The presence of small amounts of carotenoid pigments appears to increase the percentage of non-oxidative hydrolysis which produces chlorin *e* and rhodin *g*, and in general seems to decrease the destruction of the rhodins by alkali

The separation of phaeopurpurin and rhadin was actually carried out as follows. The mixture was taken to dryness and dissolved in 15 cc. of pyridine; 0.7 g. of anhydrous sodium carbonate and 0.7 g. of semicarbazide hydrochloride were added and the mixture was allowed to stand at room temperature for ten minutes. The product was transferred to five liters of ether. Extraction with 5 to 7% acid readily removed the semicarbazone of the rhodin, leaving phaeopurpurin 7 and a little high chlorin as the only other products. The yield of phaeopurpurin 7 after fractionation was 150 mg.

The phaeopurpurin 7 obtained from both of the above sources is not quite identical in physical properties with the compound prepared by hydrolysis of the dimethyl ester and whose chemical transformations were described in the fourth paper. However, it gives the same pyrolysis and saponification products.[15] It is browner in ether solution, but has the same green color in acid; the acid number is somewhat higher (10) and less sharp. A sample in ether solution was unchanged after two months. A sample of solid material after a year had changed completely to phaeopurpurin 18 and unidentifiable compounds of lower acid number. The spectrum in ether: I, 710—649; II, 545—524.5; III, 515---509484.5. E. A. 442. Order: I, III, II.

Anal. Calcd. for $C_{35}H_{38}O_7N_4$: C, 67.1; H, 6.1; N, 8.95; OCH_3, 4.95. Found: C, 67.64, 67.46; H, 6.17, 6.39; OCH_3, 4.2, 3.9.

A dimethyl ester of identical spectrum is formed on methylation with diazomethane. The acid number was 13.

Pyrolysis of Phaeopurpurin 7 from Phaeophytin.—Duplicate pyrolyses were carried out in diphenyl in nitrogen, the solution being boiled for ten minutes, then removed from the bath and swept for a further twenty minutes. Under these conditions 0.9 mol of carbon dioxide was evolved and carbon monoxide was detected in both cases. The product from 240 mg. was resolved by acid fractionation into a porphyrin fraction (8 to 9% acid) with the spectrum of isorhodoporphyrin, and a chlorin fraction with the spectrum of chlorin *f*. The yields were 17 mg. and 25 mg., respectively, and the analyses check the formulas for the monomethyl compounds in both cases. This behavior is identical with that of "synthetic" phaeopurpurin 7 and further supports the existence of a β-carbomethoxyl group in both compounds.

Anal. Calcd. for $C_{33}H_{38}N_4O_4$: C, 71.5; H, 6.9; N, 10.11; OCH_3, 5.6. Found for the chlorin: C, 71.44, 71.67; H, 7.0, 6.8; OCH_3, 5.14.

Anal. Calcd. for $C_{33}H_{36}N_4O_4$: C, 71.73; H, 6.5; N, 10.15; OCH_3, 5.62. Found for the porphyrin: C, 71.50, 71.16; H, 7.2, 7.0; N, 9.99; OCH_3, 5.25.

Hydrolysis of Phaeopurpurin 7 from Spinach Chlorophyll.—It has been shown above that the propionic ester group in methyl phaeophorbide *a* is readily hydrolyzed even in 0.04 potassium hydroxide solution at 0°. Unpublished experiments of Mr. J. L. Hartwell in this Laboratory have shown that other derivatives which contain this grouping lose the ester group with similar ease, while β-carbomethoxy ester groups are held for a much longer time. It seemed advisable therefore to carry out a mild hydrolysis under the standardized conditions. The survival of the methoxyl group (OCH_3: 5.0, 4.85) after five hours in 0.03 *N* potassium hydroxide is considered as further evi-

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[15] THIS JOURNAL, 53, 359 (1931).

dence that it is the β-carboxyl rather than the propionic acid group in phaeopurpurin 7 which is esterified.

A small sample of phaeopurpurin 7 from spinach chlorophyll was heated for five minutes with 25% potassium hydroxide in methyl alcohol in nitrogen. Like "synthetic" phaeopurpurin 7, it readily lost the bridge grouping forming chlorin f and a smaller amount of isorhodoporphyrin. Both products were identified by spectra and acid number.

Estimation of the Precursor of **Phaeopurpurin 7.**—The indicated evidence for the existence of a chlorophyll a_2 with the carbomethoxy group on the beta position of a pyrrole ring makes it important to find a convenient means of its estimation in chlorophylls of various sources, with the hope of isolating it in pure form from some favorable source. No direct method of estimation has been found thus far, due apparently to the very similar chemical and physical properties of chlorophylls a_1 and a_2. The method used involves the estimation in solution of the relative proportions of phaeopurpurins 7 and 18 formed on oxidative hydrolysis under standard conditions. The chlorophyll should be free of carotenoids which otherwise interfere with the oxidative hydrolysis One hundred milligrams of substance is dissolved in 5 cc. of pyridine and diluted with 150 cc. of ether. The solution is shaken with one-tenth its volume of 20% potassium hydroxide in propyl alcohol for eight minutes. An equal volume of ether is added and the product is transferred to it. After three to four days it is extracted with 6% acid to remove any chlorin e, then with 100 cc. extracts of 8, 10 and 12% acid until phaeopurpurin 18 begins to be extracted. The residue, when freed of carotenoids makes up the phaeopurpurin 18 fraction. The spectrum shows only very faint rhodin lines. The phaeopurpurin 7 fractions are combined and the relative proportions of both phaeopurpurins are determined by comparison with standard solutions in a comparison spectroscope.

The following percentages of phaeopurpurin 7 referred to the total phaeopurpurin concentration (7 and 18) were obtained from various sources and estimated according to the above procedure: chlorophyll from spinach 2%; commercial phaeophytin 8%; crystalline ethyl chlorophyllides (second crops from mother liquors) from Datura 10 to 23%; crude chlorophyll from marine fucus 1%; crude chlorophyll from a filamentous chlorophycea about 1%; crude methyl phaeophorbide a from phaeophytin by Willstatter's procedure 18%; methyl phaeophorbide *a* after purification by partial hydrolysis (see above) 4%; the same after two recrystallizations from acetone–ligroin 0%; free phaeophorbide a from chlorophyllides from Datura 6%.

Summary

1. Methyl phaeophorbide a may be prepared in a pure condition from methyl chlorophyllide *a*, or from phaeophytin if the first crude product is subjected to a fractional hydrolysis. The composition of pure methyl phaeophorbide a is $C_{36}H_{38}N_4O_5$.

2. After several recrystallizations, pure methyl phaeophorbide *a* yields no phaeopurpurin 7 on oxidative hydrolysis with strong alkali. With dilute alkali under oxidative conditions a monomethyl ester of chlorin g (the unstable chlorin) is formed. The carbomethoxy group of this compound has been shown to be part of the bridge grouping. This confirms the position of the methyl group in chlorophyll a assigned in Fischer's formula.

3. The precursor of phaeopurpurin 7 seems to be a second form of chlorophyll *a;* the carbomethoxy group in this compound is attached to the pyrrole ring. Evidence has been obtained indicating the existence of this second form in crude chlorophyll from a number of sources. A lactam

formula for chlorophyll *a* seems to offer the best explanation at present of the transformations of the predominant form and to allow for the existence of a second similar form with the methoxyl group in a different position.

CAMBRIDGE, MASSACHUSETTS

RECEIVED DECEMBER 27,1932
PUBLISHED FEBRUARY 9,1933

Notes

The Intramolecular Rearrangement of Phenyl Ethers with the Aid of Aluminum Chloride

BY RICHARD A. SMITH

The literature contains reports concerning the rearrangement of alkyl phenyl ethers to substituted phenols through the agencies of heat, zinc chloride; hydrogen chloride, sulfuric acid, sulfuric and glacial acetic acids, boron fluoride, etc.

Due to the fact that rearrangement of m-cresyl isopropyl ether leads to the formation of the commercially important thymol (and its isomers), this transformation has received careful study.[1] Niederl and Natelson first effected the reaction with a sulfuric–glacial acetic acid solution; the same products were obtained by Sowa, Nieuwland and Hinton using boron fluoride as the rearranging agent. The same products obtained by these workers are also obtained when aluminum chloride is used in the role of the agent favoring the intramolecular rearrangement. This agent simplifies the experimental procedure. It is believed that this type of rearrangement holds promise for further study into the interesting field of ether rearrangement, and a more comprehensive study is contemplated.

Procedure.—One mole of aluminum chloride was slowly added (twenty minutes) to one mole of m-cresyl isopropyl ether contained in a flask surrounded by a cooling bath. Heat was evolved, and the liquid became discolored. The mixture was allowed to stand for twenty-four hours and then hydrolyzed with ice water. The organic liquid which then separated was water washed and distilled. Practically all the liquid came over between 228 and 224°; it has been shown in the previous rearrangements that such a fraction consists of thymol and the para substituted isomer, *p*-isopropyl-*m*-methylphenol. The product was alkali soluble and ferric chloride colored its alcohol solution; n_D^{22} 1.5274. The yield of redistilled product was 65%. There was no unrearranged ether and no m-cresol.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
WASHINGTON SQUARE COLLEGE OF
NEW YORK UNIVERSITY
NEW YORK, N. Y.

RECEIVED OCTOBER 13, 1932
PUBLISHED FEBRUARY 9, 1933

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(1) Niederl and Natelson, THIS JOURNAL, **53**, 1928 (1931); **54**, 1063 (1932); Niederl, Natelson and Smith, Indianapolis Meeting of the American Chemical Society, 1931; Sowa, Nieuwland and Hinton, THIS JOURNAL, **54**, 2019 (1932).

The Absence of Fatty Acids Associated with Potato Starch

BY LEO LEHRMAN AND ELVIN KABAT

In the course of some work on potato starch[1] it was necessary to know the amount of fatty acid, if any, associated with the starch. Though 0.04% "fat by hydrolysis," has been reported in this starch,[2] Taylor and other workers in this field now believe that it is fat free.

To establish this point definitely we extracted a 50-g. sample of potato starch with petroleum ether for several hours and found 0.02% extraneous extractable material. Then we hydrolyzed[3] 2000 g. of the starch and found approximately 0.02% "fat by hydrolysis."

Thus potato starch does not contain fatty acids associated with it and is the best whole starch to use as carbohydrate.

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(1) The authors wish to thank Stein, Hall & Co , Inc.. N. Y. C., for their kindness in supplying this material.

(2) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920).

(3) Lehrman, *ibid.*, **51**, 2185 (1929).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
COLLEGE OF THE CITY OF NEW YORK
NEW YORK CITY

RECEIVED OCTOBER 29,1932
PUBLISHED FEBRUARY 9,1933

COMMUNICATIONS TO THE EDITOR

AN EQUATION RELATING DENSITY AND CONCENTRATION

Sir:

Redlich and Rosenfeld [Z. *physik.* Chem., **A155,** 65 (1931)] have shown on the basis of the Debye–Hückel theory that the partial molal volume of an electrolyte in dilute aqueous solution is proportional to the square root of the normality. This gives a theoretical basis for Masson's empirical rule [*Phil. Mag.*, (7) 8, 218 (1929)] connecting the apparent solution volume of a salt with its concentration in the solution.

$$\phi = \phi_0 + K\sqrt{N}$$

The relation between the concentration and density of a salt solution and the apparent solution volume of the salt can be shown to be

$$\phi = \frac{\text{Eq. Wt}}{D_{\text{H}_2\text{O}}}\text{salt} - \frac{1000}{D_{\text{H}_2\text{O}}}\left[\frac{D_{\text{soln.}} - D_{\text{H}_2\text{O}}}{N}\right]$$

By combining these two equations one obtains for the equation relating the density and normality of a solution of a strong electrolyte in water

$$D = D_0 + c_1N + c_2N^{3/2}$$

where c_1 and c_2 are constants, and D_0 is the density of pure water.

This equation was found to hold within the limits of experimental error for solutions of the alkali (without lithium) and alkaline earth halides to a concentration at least as high as 10 *N;* and for sulfuric acid to a concentration of about 25 N (75 wt. %) where there was a point of inflection. The constants c_1 and c_2 were found to be additive.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
WILLIAM C. ROOT

RECEIVED DECEMBER 6, 1932 PUBLISHED FEBRUARY 9, 1933

THE SPECIFIC SURFACE AND THE ADSORBENT PROPERTIES OF LEAD SULFATE

Sir:

1. In agreement with the results of F. Paneth and W. Vorwerk [Z. *physik. Chem.*, **101,** 445, 480 (1922)], it was found that the specific surface of lead sulfate was the same in suspensions in water as in the presence of an excess of lead nitrate. P. and V. derived an equation from which may be inferred that in the suspension of lead sulfate in water about 40% of the surface of the solid was covered with adsorbed lead ions, whereas the surface was covered with a monatomic layer of lead ions in a solution of 0.005 molar lead nitrate. We determined also the specific surface of lead sulfate in dilute solutions of sodium sulfate and found the same value as before. This constancy of the specific surface indicates that lead sulfate adsorbs neither lead ions from dilute lead nitrate solutions nor sulfate from dilute sodium sulfate solutions. This conclusion was supported by the determination of the adsorption of the two salts according to chemical methods. Considering that we worked with coarsely crystalline precipitates of lead sulfate (of the same size as those of P. and V.) it is quite possible that an adsorption takes place at the corners and the edges. If the latter would have been completely covered with adsorbed lead or sulfate ions, the adsorption would amount to less than 0.1% of the total surface of the coarse crystals, which is beyond detection by the experimental methods used.

2. The adsorption of the sodium salt of Ponceau 4R by lead sulfate was determined under various conditions. It was found that only dye ions were adsorbed, no sodium ions being removed from the solution. This means that we are dealing here with an exchange adsorption, sulfate ions being replaced by ponceau ions in the surface. Experiments are being carried out in this Laboratory with various ionic precipitates showing that the exchange adsorption occurs quite generally.

A detailed account of all the work will soon be presented for publication.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
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I. M. KOLTHOFF
CHARLES ROSENBLUM

RECEIVED DECEMBER 6, 1932 PUBLISHED FEBRUARY 9, 1933

MODIFICATION OF THE DUMAS TECHNIQUE FOR SUBSTANCES DIFFICULT TO BURN

Sir:

When a large number of nitrogen determinations by the Dumas method is to be made it is common practice to abandon the classical method, which requires emptying and refilling the combustion tube for each determination, and instead to proceed as in the determination of carbon and hydrogen, weighing the substance into a combustion boat, covering it with fine copper oxide and inserting it into the posterior end of the filled tube. This method has obvious advantages that do not need comment here. However, in the case of substances that are difficult to burn this modification may lead to low results because of incomplete combustion. In the work on the lupine alkaloids being conducted in this Laboratory it was found that some of these substances could not be analyzed in this way on account of the fact that they yielded non-volatile split products that were deposited on the walls of the tube out of contact with copper oxide and were not thoroughly oxidized.

A method for overcoming this difficulty while preserving the advantages of the general method has been developed and is here described for the benefit of those who may encounter similar difficulties. In principle the new technique involves mixing the weighed substance with a large excess of copper oxide and packing this into a metal tube which is then inserted into the combustion tube in the location ordinarily used for the combustion boat. We are using a copper tube 15 cm. long and 1.27 cm. external and 1 cm. internal diameter. The tube is ignited, cooled and filled as follows.

The forward end of this tube, which we refer to as a cartridge, is loosely plugged with a centimeter long roll of copper gauze. Upon this is poured with the aid of a solid funnel about two centimeters of previously ignited fine copper oxide,[1] then the substance mixed with copper oxide enough to form a layer of ten to twelve centimeters is poured in, the mortar is rinsed with fine copper oxide and the rinsing added to the cartridge until it is filled. It may now be inserted in the combustion tube, backed in the usual manner with a roll of oxidized copper gauze and the combustion carried out according to the classical technique.

At the conclusion of the analysis the cold cartridge may be emptied of its spent charge and if it is handled with tongs will be ready for a new charge without reignition.

Somewhat high results may be expected from the use of such a cartridge because the air adsorbed on the fine copper oxide cannot be displaced completely by the carbon dioxide stream. Blank runs, however, indicate that the error due to this factor is no greater than that encountered in the ordinary technique. The excess air due to the cartridge amounts, on the

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(1) Copper oxide is usually sufficient, but the cartridge may be filled with lead chromate or with mixtures of catalytic oxides when desirable.

average, to **0.2** cc. The results obtained by this method have been satisfactory as the following table will indicate.

Substance	% N without cartridge	% N with cartridge	Calcd.
Sparteine mercuric chloride	2.01	4.83	4.86
Alkaloid A from *Lupinus caudatus*	5.90 6.17 9.62 9.73	10.03 10 13	10.02
Alkaloid from *Lupinus cruckshanksii*	6.97 9.60	10.34 10 23	
Alkaloid from *Lupinus palmeri*	9.54 9.31	9.97 10.07	
Alkaloid from *Lupinus andersoni*	6.61 6.51	10.47	

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.
JAMES FITTON COUCH

RECEIVED DECEMBER 23, 1932 PUBLISHED FEBRUARY 9, 1933

CONCERNING THE EXISTENCE OF THE SO-CALLED HEATS OF TRANSFER (Q* VALUES) IN PELTIER HEATS

Sir:

To explain the Ludwig-Soret effect, Eastman [THIS JOURNAL, 48, **1482** (1926)] introduced the concept of the heat of transfer (Q*) [the heat of transfer of a mole of component **A** is designated as $\overline{Q}_A$ by Eastman], a latent heat which appears at some point in a homogeneous solution when a mole of dissolved component is transferred from this point to another place in the solution. The same quantity occurs in a discussion of electrolytic thermal forces. Wagner [*Ann.* Physik, (5) **3, 629** (1929)] and later Lange and co-workers [Lange and Mischtschenko, *Z.* physik. Chem., **A149,** 1 (1930)] extended these considerations to the electrolytic Peltier heats. According to them

$$ {}_{\text{metal/solution}}\pi_i = T({}_{\text{metal}}\overline{S}_i - {}_{\text{solution}}\overline{S}_i) - z_iQ^*_{\theta} - n_CQ^*_C + n_AQ^*_A \qquad \textbf{(1)} $$

(π_i is the Peltier heat given up at the anode by a mole of the potential determining ion i of valence z_i, n_C and n_A are transference numbers and Q^*_C and Q^*_A are molar heats of transfer of cation and anion).

To date the following evidence for the existence of these novel heat effects (Q*) could be advanced: **(1)** Eastman [THIS JOURNAL, 50, **292** (1928)] found a certain agreement between the Q^* values determined from Ludwig–Soret coefficients and estimated from suitable thermo-electric measurements.

(2) Thermo-electric forces between differently oriented single crystals of the same metal can only be explained by Q^* values depending on direction [Wagner, *loc. cit.*] if one does not wish to postulate a directional dependence of $\overline{S}$.

(3) Measurements of the Ludwig–Soret effect and of thermoelectric forces on solid salts and mixed crystals have been explained by use of heats of transfer [Reinhold, *Z.* physik. Chem., **B11, 321** (1931)].

All these proofs rest on measurements made on non-isothermal systems, which, because of unavoidable irreversible heat conductivity, can only be treated thermodynamically under limited conditions [cf. Boltzmann, *Sitzungsber. Akad. Wiss. Wien,* Math. Naturw. Klasse, ***96,*** **1285** (1887)].

It therefore seemed desirable to test the assumption of heats of transfer by means of electrolytic Peltier heats which can be measured isothermally [Lange and Monheim, *Z. physik.* Chem., **A150, 186** (1930)].

Peltier heats, measured with a sensitive differential calorimeter [Lange and Robinson, Chem. Rev., ***9,*** 89 (1931)] of the system $Ag/AgNO_3$ confirmed more exactly than previously the validity of the Thomson relationship between Peltier heat (a) and thermo-electric force (ϵ)

$$\pi/T = \epsilon$$

for electrolyte systems, so that objections raised against the non-isothermal foundations mentioned above have been weakened [Lange and Hesse, *Z. Elektrochem.,* 38, **428** (1932)].

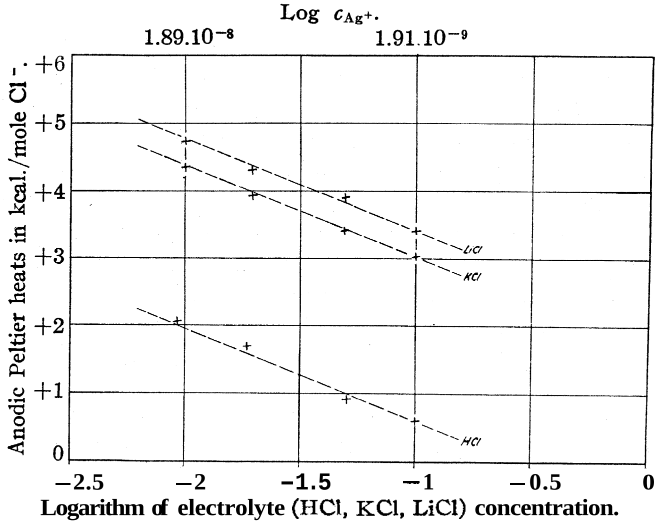

Fig. 1.—Electrolytic Peltier heats of the system $Ag/AgCl/HCl$ (KCl, $LiCl$).

Peltier heats were also measured at 25° for the system $Ag/AgCl/Cl^-$ in the presence of different cations (K^+, H^+, Li^+).

According to equation (1) it follows for equal Cl^- concentration that

$$ {}_{AgCl/KCl}\pi_{Cl^-} - {}_{AgCl/HCl}\pi_{Cl^-} = T({}_{HCl}\bar{S}_{Cl^-} - {}_{KCl}\bar{S}_{Cl^-}) $$
$$ + ({}_{HCl}n_{H^+}Q^*_{H^+} - {}_{KCl}n_{K^+}Q^*_{K^+} + {}_{KCl}n_{Cl^-}Q^*_{Cl^-} - {}_{HCl}n_{Cl^-}Q^*_{Cl^-}) $$

A more exact discussion shows that the first term on the right is practically zero for the small concentrations of the investigation. Therefore without consideration of the Q* terms the electrolytic Peltier heats should be equal within the limits of experimental error for the different electrolytes.

As a matter of fact there are appreciable differences (almost 3 kcal.) even in 0.01 *M* solutions as the figure shows.

The existence of and therewith the necessity for considering these Q* terms which Eastman introduced is thus established. It is also evident that the differences of partial molar entropies can not be determined by employing Peltier heats and thermo-electric forces alone [*cf.*, on the contrary, Bruzs, Z. *physik. Chem.*, A161, 83 (1932)].

A more detailed presentation of this material will be published shortly in a German journal.

PHYSICAL CHEMISTRY LABORATORY
OF THE UNIVERSITY
ERLANGEN, GERMANY

E. LANGE
TH. HESSE

RECEIVED JANUARY 6, 1933 PUBLISHED FEBRUARY 9, 1933

THE THERMAL INTERCONVERSION OF MIXED BENZOINS

Sir:

Julian and Passler [THIS JOURNAL, 54,4756 (1932)] record another case of the transformation of the mixed benzoin not formed by the cyanide condensation (anisbenzoin) into the isomer formed by the cyanide method (benzanisoin). The reverse transformation, which is the object of our work, has not hitherto been recorded The present writers have found that pure benzanisoin (cyanide condensation), after heating for three hours at 125–130° and fractionation from cold dilute alcohol, gives appreciable amounts of anisbenzoin, m. p. 89°, identical with Asahina and Terasaka's compound. Evidently, above the melting point, an equilibrium lying far over to the side of benzanisoin exists. The amount of pure anisbenzoin isolated, after heating, from 20 g. of benzanisoin was 0.10 g. but considerably more was present.

EXPERIMENTAL RESEARCH LABORATORIES
BURROUGHS WELLCOME AND CO.
TUCKAHOE, N. Y.

JOHANNES S. BUCK
WALTER S. IDE

RECEIVED JANUARY 9, 1933 PUBLISHED FEBRUARY 9, 1933

THE NEUTRON, THE ATOMIC NUCLEUS AND MASS DEFECTS

Sir:

Two general theories of the constitution of atomic nuclei have been proposed: (1) that the nucleus is built up largely from a-particles (Harkins and Wilson[1]) and (2) that the Harkins–Masson[2] nuclear formula $(p_2e)_z(pe)_I$ (a), $(np)_z n_I$ (b) or $(\alpha/2)_z n_I$ (c), represents the constitution of any nucleus

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(1) (a) Harkins and Wilson, *Proc. Nat. Acad. Sci.*, 1, 276 (1915); (b) THIS JOURNAL, 37, 1368, 1383 (1915).

(2) (a) Harkins, THIS JOURNAL, 42, 1956 (1920); *Phil. Mag.*, 42, 306 (1921). See also Ref. 1(b) and Durrant, THIS JOURNAL, 39, 621–7 (1917). (b) Masson, *Phil.* Mag.

(Heisenberg.[3] See also the earlier paper of Iwenko[4]). Here p represents a neutron; e, an electron; n, a neutron; a, an a-particle, and z and I, the atomic and isotopic numbers. Form (b) of the formula expresses the Heisenberg theory best, though he does not deny the existence of a-particles in the nucleus. Obviously the total number of neutrons is

$$N = Z + I$$

in which Z gives the number of neutrons combined with protons, and I the number of "extra" neutrons.

The energy of binding of (a) a proton and electron to give a neutron is one million electron volts, of (b) a neutron and proton to give H^2 is also one, while that of two H^2 atoms to give one helium atom is 23 million electron volts (Table I). The values for (a) and (b) are uncertain, but the sum is $1.91 \cdot 10^6$.

Thus the pairing of the neutrons and extra protons in the helium nucleus involves a binding energy twelve times as great as the sum of the binding energies of (1) a proton and an electron, and (2) of a neutron and a proton.

Thus if a neutron enters into an a-particle it is subjected to such ex-

TABLE I

BINDING ENERGY OF ATOMS IN 10^6 ELECTRON VOLTS

$$\left.\begin{array}{ll} p + e \longrightarrow n_2 & 1.(?) \\ n + p \longrightarrow H^2 & 1.\ (?) \end{array}\right\} \text{Sum} = 1.91$$

$$2p + e \longrightarrow H^2 \quad 1.91$$

	Proton		Neutron		H^2	
	Odd	Even	Odd	Even	Odd	Even
$2H^2 \longrightarrow He$						23.2
$He + H^2 \longrightarrow Li^6$					3.42	
$Li^6 + n \longrightarrow Li^7$			6.2			
$Li^7 + H \longrightarrow 2He$		14.0				
$B^{10} + n \longrightarrow B^{11}$			6.3			
$B^{10} + H^2 \longrightarrow C^{12}$						21.0
$B^{11} + H \longrightarrow C^{12}$		14.1				
$C^{12} + n \longrightarrow C^{13}$			5.7			
$C^{12} + H^2 \longrightarrow N^{14}$					8.5	
$C^{13} + H \longrightarrow N^{14}$		(4.0)[a]				
$N^{14} + H^2 \longrightarrow O^{16}$						20.0
$O^{16} + n \longrightarrow O^{17}$			3.2			
$O^{16} + 2H^2 \longrightarrow Ne^{20}$						(12.4 av.)
$F^{19} + H' \longrightarrow Ne^{20}$		6.8				
$Ne^{20} + 2n \longrightarrow Ne^{22}$				(4.2 av.)		
$Ne^{22} + H \longrightarrow Na^{23}$	9.3					
$A^{36} + 4n \longrightarrow A^{40}$				(7.4 av.)		

[a] This value is not directly comparable with the others in this column, since it relates to the formation of a nucleus which does not contain a whole number of a-groups.

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(3) Heisenberg, *Z. Physik*, **77**, 1 (1932); **78**, 156 (1932).

(4) Iwenko. *Nature*, **129**, 798 (1932).

tremely powerful forces of polarization that if it does not entirely lose its individuality it becomes very different from a neutron not thus combined.

Table I also gives the approximate binding energy for the union of any atom listed in column I with a proton, neutron, or H^2 nucleus. Column 6 shows that the binding energy for the union of an $\alpha/2$ group is much larger (value about 20 million volts) if the final number of such groups in the nucleus is even, than if this number is odd (from 3 to 9 million volts). If the final number is even, then the last p_2e group presumably forms an a-particle with the odd p_2e group already present. Relatively high values are also found for the completion of an a-particle, by a proton (column 3, about 14 million volts for Li^7 and B^{11}, though only 6.8 for F^{19}). No data are available for the calculation of the binding energy for a single neutron in any case in which the final nucleus presumably consists of α-particles alone.

TABLE II

MASS DEFECT OR BINDING ENERGY PER &-PARTICLE

$m' = \frac{-\Delta m}{N\alpha} \times 10^4$		$\frac{-\Delta m'}{N\alpha} \times 10^4$
C^{12}	10	12
O^{16}	22	0
Ne^{20}	22	
. . .	. .	
A^{36}	48	3
A^{40}	51	4
Cr^{52}	62	−0.3
Zn^{64}	61	−0.5
Kr^{80}	59	−1.0
Sn^{112}	51	−2.6
Xe	43	

Table II is of interest since it shows that the mass defect per a-particle rises rapidly with the number of a-particles contrary to the assumption of Gamow's formula,[5] up to mass 52 (assumed number of a-particles = 13) and then decreases slowly with the mass number. There is no apparent discontinuity in the values where, between A^{36} and A^{40} according to theory (1) the first pair of cementing or "free" electrons enters, or theory (2) the first set of "free" neutrons (4 in number) come into the nucleus.

In a later paper the two theories will be compared on the basis of the above and other relations. In this connection, the mass numbers for magnesium, silicon, sulfur and calcium are badly needed, but are not at present available.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO. ILLINOIS

WILLIAM D. HARKINS

RECEIVED JANUARY 14, 1933 PUBLISHED FEBRUARY 9, 1933

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(5) Gamow, "Constitution of Atomic Nuclei and Radioactivity," Oxford, 1931.

THE ATOMIC WEIGHT OF CESIUM

Sir:

Some years ago about four kilograms of cesium nitrate was extracted from pollucite and fractionally crystallized in the hope of concentrating an alkali element of higher atomic weight [Baxter, THIS JOURNAL, 37, 286 (1915)]. This hope was not realized. A part of the fourth and fifth less soluble fractions of the last (18th) series of this crystallization which together amounted to 1200 g. have been further purified by three crystallizations as perchlorate, and, after conversion to chloride and fusion, by three crystallizations as chloride, all in platinum. The product was tested spectrographically in an arc formed by pure copper electrodes and was found to be wholly free from rubidium and potassium so far as could be seen. Analysis was then carried out by fusing the chloride in a weighed platinum boat in a quartz bottling apparatus and then comparing the salt with silver nephelometrically. In Analyses 1 and 2 the fusion atmosphere was nitrogen, in Analyses 3 and 4 the fusion atmosphere was hydrogen containing a small proportion of hydrogen chloride, while in Analysis 5 it was hydrogen only. The close agreement of the results seems to indicate that cesium chloride shows no tendency to become basic under these conditions nor to retain hydrogen chloride.

THE ATOMIC WEIGHT OF CESIUM

Analysis	CsCl in vacuum, g.	Ag in vacuum, g.	Ratio CsCl:Ag	Atomic wt. of cesium
1	8.96291	5.74296	1.56068	132.91
2	9.60983	6.15751	1.56067	132.91
3	9.70288	6.21686	1.56074	132.92
4	9.53125	6.10708	1.56069	132.91
5	7.52304	4.82025	1.56072	132.91
		Average	1.56070	132.91

The atomic weight found in our experiments is about 0.1 unit higher than that found by Richards and Archibald [Proc. *Am. Acad.* Arts *Sci.*, 38, 443 (1903)] and Richards and Françon [THIS JOURNAL, 50, 2162 (1928)], a difference which we can explain only by suggesting that the material used by these experimenters may not have been wholly free from rubidium and potassium, only 0.2% of even the former of which would be necessary to explain the discrepancy.

It is interesting that Aston [Proc. *Roy. Soc.*, (London) A134, 571 (1932); Phil. *Mag.*, 42, 436 (1921)] and Bainbridge [*J.* Franklin *Inst.*, 212, 317 (1931)] agree that cesium is a simple element and that Aston calculates from measurements of its packing fraction (-5×10^{-4}) an atomic weight of 132.917, using the conversion factor, 1.000125. With the factor 1.00022, cesium becomes 132.904. Our result therefore appears to remove the chief discrepancy between atomic weights determined by physicochemical methods and those obtained from mass-spectrographic data.

We expect to continue work on this problem.

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G. P. BAXTER
J. S. THOMAS

RECEIVED JANUARY 18, 1933 PUBLISHED FEBRUARY 9, 1933

THE HABER–WILLSTÄTTER CHAIN MECHANISM OF ORGANIC AND ENZYMATIC PROCESSES

Sir:

Haber and Willstatter [*Ber.*, 64, 2844 (1931)] have proposed chain mechanisms for a number of organic and enzymotic processes of which we may cite the oxidation of alcohol as typical. Their reaction scheme is

$$CH_3CH_3OH + \text{Enzyme} = CH_3\overset{/}{C}H(OH) + \text{Mono desoxy-enzyme} + H^{\cdot} \qquad \text{(a)}$$

$$CH_3\overset{/}{C}HOH + CH_3CH_2OH + O_2 = 2CH_3CHO + H_2O + OH \qquad \text{(b)}$$

$$OH + CH_3CH_2OH = CH_3\overset{/}{C}HOH + H_2O \qquad \text{(c)}$$

A similar chain can be set up for aldehyde oxidation. We have attempted to verify such a mechanism, starting the chain of processes at stage (c) by decomposing hydrogen peroxide photochemically in mixtures of alcohol and oxygen suitably agitated. We find that the photo-decomposition of peroxide markedly sensitizes the interaction of alcohol and oxygen. The oxidation process is a chain reaction, sensitive to inhibitors but the chain length is short. It is much shorter than the assumed chain length ($\sim 10^5$) in the communication of Haber and Willstatter. Dilute aqueous aldehyde solutions behave similarly and the chain length is somewhat longer. The detailed results will be communicated immediately.

DEPARTMENT OF CHEMISTRY
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PRINCETON, N. J.
HUGH S. TAYLOR
AUSTIN J. GOULD

RECEIVED JANUARY 20, 1933 PUBLISHED FEBRUARY 9, 1933

ORIENTATION IN THE FURAN NUCLEUS

Sir:

The introduction of an aldehydic group into 3-methylfuran, by means of hydrogen cyanide and hydrogen chloride, results in the formation of 3-methyl-2-furfural [Reichstein, Zschokke and Goerg, Helv. *Chim. Acta,* 14, 1277 (1931)]. The nitro-p-methylfuran obtained from 3-methylfuran by the action of fuming nitric acid in acetic anhydride has been shown to be 3-methyl-2-nitrofuran [Rinkes, Rec. trav. *chim.*, 49, 1125 (1930)] by comparison with an authentic specimen kindly provided by Dr. I. J. Rinkes.

The 3-methylfuran was synthesized by the following sequence of reactions: 3-furoic acid ⟶ 3-furoyl chloride ⟶ 3-furaldehyde ⟶ 3-furaldehyde-hydrazone ⟶ 3-methylfuran. It readily forms a chloromercuri compound (3-methyl-2-furylmercuric chloride) which melts at 142°, and such mercurials are recommended as satisfactory derivatives for the characterization of many furan compounds, including those with an α-carboxylic group [*Rec. trav.* chim., 51, 1054 (1931), and 52 (March) (1933)].

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
ROBERT R. BURTNER

RECEIVED JANUARY 23, 1933 PUBLISHED FEBRUARY 9, 1933

THE EFFECT OF WATER ON THE PHOTOSYNTHESIS OF HYDROGEN CHLORIDE

Sir:

In the last few months several papers have questioned the necessity of having water vapor present in order to bring about the photochemical union of hydrogen and chlorine in visible light [Rodebush and Klingelhoefer, THIS JOURNAL 55, 130 (1933); Kimball and Eyring, ibid., 54, 3876 (1932); Allmand and Craggs, *Nature,* 130, 927 (1932)]. Coehn and Jung [Z. *physik. Chem.,* 110, 705 (1924)] reported several years ago that the reaction would not proceed if the water vapor pressure was reduced below 10^{-7} mm., and the maximum rate was not attained unless the water vapor exceeded 10^{-5} mm. In order to test this observation it is obvious that great care must be taken to prevent the accidental entry of sufficient water to cause the reaction to go. The most certain method is to carry out the experiments with the entire reaction vessel at such a temperature that the equilibrium value for the water vapor pressure is within the desired limits. We have performed such experiments at various temperatures between 145 and 200°K. and we find no evidence of the falling off in the rate such as reported by Coehn and Jung. If we had confirmed their results, there should have been a marked decrease in the rate between 160 and 177°K. In a recent note Baker [*Nature,* 131, 27 (1933)] claims to have demonstrated the effect of water on this reaction as a lecture experiment. As he used phosphorus pentoxide to dry his gases the results he observed must have been due to inhibitors introduced by this reagent. We feel that our results show definitely that water vapor has no effect on the rate of photosynthesis of hydrogen chloride.

In our experiments the reaction vessel was a Pyrex glass bulb placed in a lead block provided with a Pyrex window. This ensemble was suspended in a Dewar vessel and cooled by means of liquid air and a cold air blast. Resistance thermometers wound on the reaction vessel and the lead block permitted accurate measurements of the temperature. In the temperature range covered, liquid or solid chlorine was present in the reaction vessel and therefore the rate could be followed by observing the pressure change.

At the present time we are investigating the rate law over the temperature range mentioned above. Preliminary results indicate that the dependence on the light absorbed changes from the first power to the square root as the temperature is lowered.

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NEW BOOKS

Hundert Jahre **Liebigs** Annalen der Chemie. (One Hundred Years of **Liebig's** Annalen der Chemie.) By RICHARD WILLSTATTER. Verlag Chemie, G. m. b. H., Corneliusstrasse **3,** Berlin W 10, Germany, **1932.** 12 pp. **14 × 22** cm.

The appearance during December, **1932,** of the 500th volume of Liebig's *Annalen der Chemie* is **a** significant event in the life history of our science. This periodical, founded by Liebig just one hundred years ago, has had in the past as editors a succession of the great organic chemists of Germany—Wohler, Kopp, Hofmann, Kekulé, Erlenmeyer, Volhard, Fittig, Von Baeyer, Wallach, Fischer, Graebe and Zincke. Today its editorial board consists of Willstatter, Wieland, Windaus and H. Fischer—every one of them a Nobel Prize laureate. In the pages of the *Annalen* are to be found a large proportion of the great classics of organic chemistry. Its five hundred volumes constitute substantially a history of the development of that science.

What other scientific journal has so inspiring a past and so brilliant a present!

ARTHUR B. LAMB

An Introduction to Chemistry. By FRANK B. KENRICK, Professor of Chemistry in the University of Toronto. The University of Toronto Press, Toronto, Canada, **1932.** viii + **434** pp. **33** figs. 15 X 23 cm. Price, $3.00.

Not since Ostwald's attempt, a quarter of a century ago, to account for the fundamental laws of chemistry without the use of the atomic theory, has appeared a more interesting and consistent development of the principles of the science from actual laboratory observations than in "An Introduction to Chemistry" by Professor Kenrick. It is difficult to believe that in these days elementary students will "struggle" (to use the author's own word) with the labored and involved presentation of the subject, which is necessary when all terms and conceptions which are not rigidly defined by experiment are abandoned. It is equally difficult to believe that teachers will consider that a student **can** afford the time to master, for example, one hundred and forty-five difficult pages, in order to get the distinction between mechanical mixtures, solutions and pure substances. In short, to quote directly from the preface, "This will not be found to be a 'teachable' book; a teachable book must be a learnable book, and that is a most dangerous educational weapon. Chemistry is not a teachable subject; it is a thing to be struggled with."

If, however, this book is to be viewed, not as one to be used by a beginner, but as a protest by the author against the current elementary books, which are top-heavy with theory and riddled with vague and ambiguous terms, then it should be commended to those who can appreciate its significance and especially to teachers of elementary chemistry. A brief description of the processes of the manufacture of salt, chlorine and caustic soda, and of the refining of crude sugar and accounts of the compositions of wood, of air, and of rocks, serve as illustrative material for the interpretation in laboratory terms of a number of the common chemical words, such as constituent, dissolved constituent, composition, solution, pure substance, element, atomic weight, molecular weight, chemical formula, ion, dissociation and some others.

The meaning of the term "constituent," for example, is developed with great care and at some length, since it is constantly referred to throughout the book. "A set of constituent substances of a material" is defined as "either a set of substances into which the material can be turned quantitatively or a set from which it can be made quantitative" This definition leads to the description of 26% brine as having eight different sets of constituents depending upon the point of view—namely, (1) salt + water, (2) concentrated hydrochloric acid + 32.5% caustic soda solution, (3) oxygen + hydrogen + salt, (4) chlorine + hydrogen + cell liquor, (5) chlorine + hydrogen + water + salt + caustic soda, (6) chlorine + hydrogen + water + caustic soda, (7) chlorine + hydrogen + water + oxygen + sodium, (8) chlorine + oxygen + hydrogen + sodium. While it must be granted that the term "constituent" is commonly used with different meanings in different connections, it does not seem to the reviewer to add to the clarity of the situation to say that the constituents of brine are solutions of hydrochloric acid and of caustic soda.

The strictly logical derivations of many other terms as based upon experimental observations lead to equally unusual definitions, which the reader is at first inclined to challenge. The book is thus most stimulating. While it is true that the meanings of many of our most common words, such as acid, are vague, the cumbersome phraseology of precise usage, which often involves long parentheses, is frequently unnecessary and confusing. This insistence on precision in all cases is not unlike a demand that all weighings should be made with the utmost accuracy, whether or not the final figures have significance So, in some instances, the author of this book may be open to criticism as to his sense of proportion.

In conclusion, the book is a most timely reaction against the current looseness of phrase and thought which has wandered too far into theory and away from experimental facts. If, in turn, this book may have gone too far in the other direction to be a practical textbook, yet a careful reading of it should have a most desirable influence on the thoughtful students and teachers of the principles of chemistry.

KENNETH L. MARK

The **Structure** of Molecules. Edited by P. DEBYE. Authorized Translation by Winifred M. Deans, M.A., B.Sc. Blackie and Son, Ltd., **50** Old Bailey, London, E. C. 4, England, **1932.** xii + 190 pp. **14.5 X 21.5** cm. Price, 15/-.

This is a collection of the papers presented at the fourth summer conference at Leipzig (1931), introduced by a two-page preface by Debye. The first paper, by Wolf, Bodenheimer and Herold, presents a qualitative discussion of rotation about valence bonds together with applications of the concept of hindered rotation to the relative yields of optical isomers obtained in a number of type reactions. This is followed by an account of the experimental results of the study of the band spectra of polyatomic molecules by Mecke, in which the classification and notation of normal vibrations receive special attention. Rasetti offers a brief treatment of the theory of the Raman effect and of the experimental technique employed in the study of this effect in crystals. In the succeeding paper Placzek presents a detailed mathematical analysis of the intensities and polarizations of Raman lines obtained from molecules of various symmetry types. The application of band spectra to the study of the dissociation of diatomic molecules is discussed by Sponer. Predissociation is reviewed in two papers, the first, by Henri, containing a large amount of experimental data, and the second, by Kronig, presenting a brief theoretical discussion of the topic. The concluding paper, by Herzberg, deals with that branch of the recent additions to the theory of valence which has been developed chiefly by Nund, Mulliken and Herzberg, and which will apparently be of more value to the band spectroscopist than to the chemist.

The papers vary somewhat in scope, but for the most part they are rather more comprehensive than the usual seminar report and less so than the average article of the review journals They are not well suited to those unfamiliar with the topics discussed, but to the fairly advanced student they offer interesting and suggestive discussions of the several subjects. It is only natural that these discussions should be strongly colored by the personal interests of the authors. A small proportion of the material has not been published elsewhere, except in the German original.

The work of translation has, on the whole, been well done, but one is led to question the desirability of translating books of this type both because the majority of their readers would prefer the original, and because the time consumed in translation is a considerable portion of such books' periods of usefulness.

HUGH M. SMALLWOOD

Fixed Nitrogen. Edited by HARRY A. CURTIS. American Chemical Society Monograph. The Chemical Catalog Company, Inc., **419** Fourth Ave., New York, **1932. 517** pp. ***82*** figs. **15.5** X **23.5** cm. Price, **$12.00.**

To one interested in the question of nitrogen fixation, this volume on Fixed Nitrogen, edited by Harry A. Curtis, being No. 59 of the American Chemical Society Monograph Series, will prove a welcome and ready means of obtaining at once a fairly up-to-date record, both theoretical and practical, for such it is. Dr. Curtis himself, the author of four general introductory chapters covering the history, sources and utilization of fixed nitrogen, the Chilean nitrate industry, and fixed nitrogen from coal, chose well his collaborators, They were chosen from the research staff of the Fixed Nitrogen Research Laboratory or from past members of the staff who have served an important apprenticeship there. No one can read their contributions without admiration for the thoroughness of the work done.

The reviewer has found nothing to criticize and much to praise. The whole plan of the book has been under each chapter to give the most modern development with a discussion of the theory upon which that development has been made and by which it is stil! guided. Careful reference has also been given to the best literature on each topic so that the student who desires more detail can readily obtain it.

"The Arc Method of Nitrogen Fixation" has been covered by Norman W. Krase; "Synthetic Ammonia," by P. H. Emmett; "The Cyanamide Method of Nitrogen Fixation" and the "Synthesis of Urea," by H. J. Krase; and "The Alkali Cyanide Method of Nitrogen Fixation," by E. W. Guernsey. The chapter "Nitrogen Fixation by Living Organisms," by F. E. Allison, gives, too, a careful résumé of this subject, through which nitrogen is made available in soil. Aside from these specific topics, C. H. Kunsman and Richard Wiebe have important chapters covering the important role which physics has played in the problem, with the physical properties of the gases involved and the studies of catalytic surfaces. An important chapter on "High Pressure Equipment and Technic," by J. R. Dilley and W. L. Edwards, will be of special importance to the mechanical engineer interested in this subject, not only in its application to nitrogen fixation but in other fields. The chapter reproduces detailed drawings to scale, clearly showing some of the mechanics by which the difficulties incident to high pressure have been overcome. The book closes with a chapter on "Synthetic Nitrogenous Fertilizers." by Wm. H. Ross and Albert R. Merz, and a chapter on "Nitrogen Statistics," by P. E. Howard.

The book is well written and the typography is a credit to the series to which it belongs.

The reviewer realizes that the statement he has given is little more than a restatement of the table of contents, but the book is so replete with information, so well illustrated, so entirely up to date theoretically and practically, that nothing else is possible within the limits available to him. He has no hesitancy whatever in recommending the book as having no equal in the field which it covers, *viz.*, that of the fixation of nitrogen.

CHARLES L. PARSONS

BOOKS RECEIVED

December 15, 1932–January 15, 1933

KENNETH C. BAILEY, Editor. "The Elder Pliny's Chapters on Chemical Subjects." Part I, with Translation and Notes. Longmans, Green and Co , 55 Fifth Ave., New York. 249 pp. $5.00.

HORACE G. **DEMING**. "Introductory College Chemistry. An Elementary Course Developed Historically." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 590 pp. $3.00.

I. M. **KOLTHOFF** AND HARRY **FISCHGOLD**. "Same-Basen-Indicatoren. Ihre Anwendung bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration." Gleichzeitig Vierte Auflage von "Der Gebrauch von Farbindicatoren." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany 416 pp. RM. 18.60; bound, RM. 19.80

WILLIAM ALBERT **NOYES** AND W. ALBERT **NOYES**, JR. "Modern Alchemy." Charles C. Thomas, Publisher, 300 East Monroe St., Springfield, Ill. 207 pp. $3.00.

WO. OSTWALD, Editor. "Filme und Fäden." Sonderheft der *Kolloid-Zeitschrift*, Band LXI, Heft 2. Hauptvortrage Gehalten auf der IX Hauptversammlung der Kolloid-Gesellschaft im Mainz, vom 28–30 September, 1932. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 184 pp RM. 12.

HANS RUPE. "Adolf von Baeyer als Lehrer und Forscher. Errinnerungen aus seinem Privatlaboratorium." Verlag von Ferdinand Enke, Stuttgart, Germany 26 pp. RM 2.50.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Gaseous Oxygen in the Thermal Reaction between Manganic Ion and Oxalate Ion

BY HERBERT F. LAUNER

Introduction

During the study of the kinetics of the reaction between permanganate ion and oxalate ion by a manometric method,[1] it was found that at higher concentrations of oxalate ion, the rate of pressure increase was lower when oxygen was present than when oxygen was absent from the gas space above the solution. Although the nature of the effect was not appreciated at that time, care was taken to select conditions under which the effect did not manifest itself, or under which the effect of changing the concentration of the various reacting substances was essentially the same in the presence or absence of oxygen.

Several investigators[2] have observed a relationship between the partial pressures of oxygen and the rates of chemical reactions similar in type to the present one. No attempt was made, however, to explain the phenomena except on the basis of a highly specific deactivating property ascribed to oxygen.

The writer believes that in the present article the role of oxygen in the manganic-oxalate reaction is explained on a purely chemical basis.

Apparatus and Experimental Method

The reaction rates were studied manometrically in an apparatus previously used by the writer, with a few minor modifications.[1] Arrangements were made for freeing the reaction mixtures from oxygen by passing a rapid stream of purified nitrogen through the violently agitated solutions containing all but one component, the potassium oxalate. This was continued for thirty minutes, during which time the temperature of the solution was maintained at 40°. After recooling to 25.01 ± 0.03°, the temperature at which all rate measurements were made, the last reactant, previously freed from oxygen in the same manner and kept under purified nitrogen at all times, was introduced. The system was then closed and pressure changes above or below atmospheric were read on the water manometer.

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(1) Launer, THIS JOURNAL, 54, 2597 (1932).

(2) Jodlbauer, Z. *physik. Chem.*, 59, 513 (1907); Roseveare and Olson, THIS JOURNAL, 51, 1717 (1929); Roseveare, *ibid.*, 52, 2612 (1930).

The nitrogen was taken from a cylinder and was purified by passing first through a spiral wash bottle containing fresh alkaline pyrogallol solution, and then over bright copper turnings maintained at a temperature slightly below the softening point of Pyrex glass.

The solutions were saturated with oxygen by passing this gas, previously freed from carbon dioxide, through the violently agitated solutions for five minutes. The solutions were saturated with air merely by allowing them to come to temperature in the apparatus.

The carbon dioxide was determined at the end of the experiments by passing air freed from carbon dioxide, through the violently agitated solutions maintained at 40°, for thirty minutes. This then passed through a special spiral absorption bottle, which could be completely dismantled, containing a known quantity of standard 0.2 *N* sodium hydroxide. An excess of barium chloride solution was then added and the mixture titrated with standard hydrochloric acid using phenolphthalein. The accuracy possible by this method is shown in the next paragraph.

For purposes that will be apparent below, the Henry's law constant for carbon dioxide for these solutions was determined. Weighed quantities of pure sodium carbonate were sealed in capsules of very thin glass. These were introduced into typical reaction mixtures containing everything but the oxidizing agent. After the capsule had been broken in the closed system, the pressure became steady at its final value in less than one minute, incidentally showing the suitability of the apparatus. The carbon dioxide was then determined by the above method. These data are recorded in Table I

TABLE I

Na_2CO_3, g.	Press. CO_2, cm. H_2O	Mg. of CO_2 (calcd.)	Mg. of CO_2 found	Ratio press. CO_2/wt. CO?
0.0545	66.6	22.6	23.4	2.95
0.0429	52.4	17.8	18.3	2.95

In order to study the pressure changes due to the absorption of oxygen, it was necessary to eliminate the carbon dioxide upon formation. For this purpose, a small, horseshoe-shaped metal tray, coated with paraffin and containing 2 g. of well granulated sodium hydroxide, was placed in the gas space out of reach of the solution. It was found that by this device carbon dioxide was absorbed twice as rapidly as was necessary for the most rapid reaction studied.

The volume of the gas space was determined for all experiments to be 107 cc., by forcing a known volume of water into the closed system (already containing 100 cc. of water) and noting the pressures concerned. The volume of the liquid phase was always 100.0 cc.

The final pressures were obtained by heating the solutions to 50° and recooling.

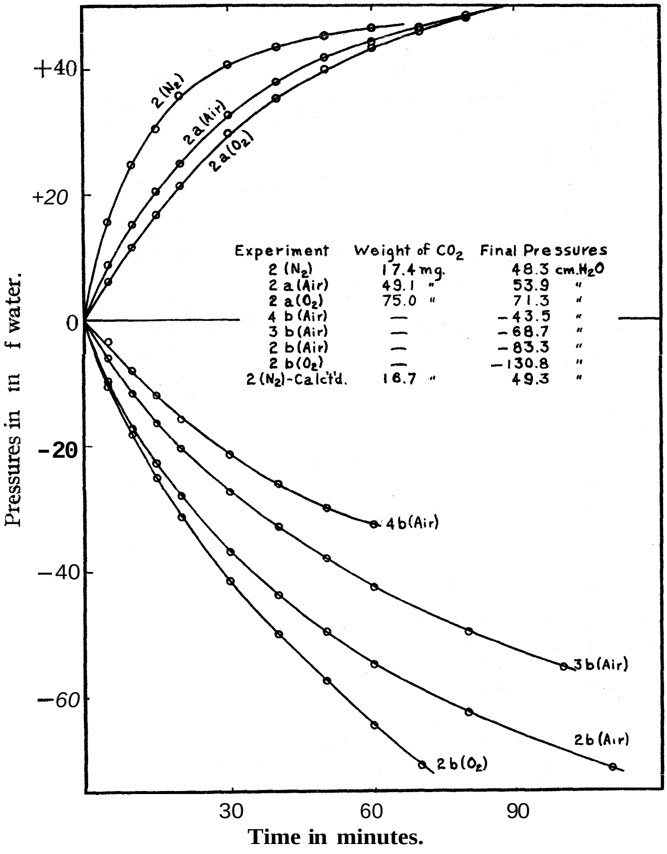
"C. P." quality chemicals were used throughout.

Preliminary Discussion

The greater part of the rate data is grouped at the end of this article.

For the purpose of clarity the principal results of the investigation will be presented and discussed at this point. When in contact with only pure nitrogen, a solution containing manganic, manganous, oxalate and hydrogen ions, among other substances, at given concentrations lost its deep cherry-red color arising from tripositive manganese and became colorless in approximately fifty minutes. During this time the pressure had increased at a rate represented by curve 2 (N_2), Fig. 1, below, and the final pressure was 48.3 cm. of water, as noted on Fig. 1. The weight of carbon dioxide was found to be 17.4 mg., which figure agrees well with 16.7 mg., the weight of carbon dioxide calculated from the amount of oxidizing agent added.

When an identical solution was in contact with air, color **was** still definitely visible after one hundred and ten minutes, and the curve 2a (Air), Fig. 1, representing the rate of pressure increase, lay below $2(N_2)$ for approximately seventy minutes. The final pressure became, however, **53.9** cm. of water, the difference not to be accounted for by experimental error. Furthermore, the weight of carbon dioxide in experiment 2a (Air) was found to be 49.1 mg. It was assumed, therefore, that oxygen had acted as a co-oxidizer to produce the additional carbon dioxide.



Experiment	Weight of CO_2	Final Pressures
$2 (N_2)$	17.4 mg.	48.3 cm. H_2O
2 a (Air)	49.1 "	53.9 "
$2 a (O_2)$	75.0 "	71.3 "
4 b (Air)	—	-43.5 "
3 b (Air)	—	-68.7 "
2 b (Air)	—	-83.3 "
$2 b (O_2)$	—	-130.8 "
$2 (N_2)$-Calc'd.	16.7 "	49.3 "

Fig. 1.—The effect of oxygen.

This assumption was borne out by the following experiment, called 2b (Air). Experiment 2a (Air) was repeated, except that the small tray containing the sodium hydroxide was placed in the gas space. The sodium hydroxide absorbed the carbon dioxide, and thus any oxygen absorbed during the manganic–oxalate reaction caused a decrease in pressure. The rate of this pressure decrease is represented by curve 2b (Air), Fig. 1, the final pressure being **−83.3** cm. of water.

Since oxygen was absorbed also in experiment 2a (Air), it is an obvious and necessary conclusion that the true pressures of carbon dioxide in experiment 2a (Air) at any given time may be calculated by combining the data of experiments 2a (Air) and 2b (Air), thus giving curve 2ab (Air), shown below in Fig. 2.

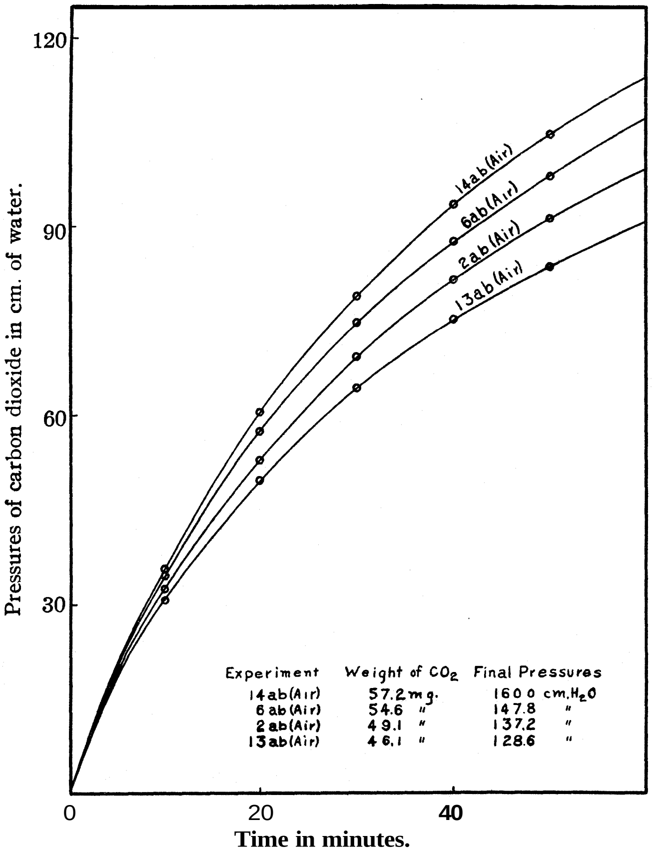


Fig. 2.—The effect of manganous ion.

It should be mentioned in this connection that solutions containing manganous ion, oxalate ion, acid, etc., under the same conditions as above, but containing no manganic ion, did not react at a measurable rate with oxygen.

These facts reveal the following rather unusual situation. If the rate of the manganic–oxalate reaction be studied by determining the amount of carbon dioxide formed, the rate of the reaction will, under certain conditions, appear much higher in the presence of oxygen than in its absence.

On the other hand, the rate of the reaction will appear much lower in the presence of oxygen than in its absence, if the rate be crudely measured by noting the large differences in color after fifty minutes or, more exactly, by titrating iodimetrically the tripositive manganese. This longer persistence of the color due to tripositive manganese when oxygen is present is shown by experiments below, the writer believes, to be due to the regeneration of manganic ion by a peroxide of carbon reacting with manganous ions to produce manganic ions.

The Experiments and Discussion

The compositions of all of the reacting mixtures are given in Table II, below Fig. 1. Since all experiments whose titles begin with the same number have identical liquid composition (except with regard to the dissolved gas), the composition of this mixture will be given in Table II opposite that number. For example, the compositions of the solutions for experiments 2(N_2), 2a (Air), 2b (Air), 2a (O_2) and 2b (O_2) are identical and are given simply opposite the number 2.

The notations (N_2) and (O_2) signify that only pure nitrogen or pure oxygen, respectively, besides water vapor was present in the gas space at the beginning of the experiment. The letter "b" signifies that the carbon dioxide absorber was in position in that experiment. The letter "a" signifies that the partial pressures of all gases were operating and hence the values of pressure were due not only to carbon dioxide produced, but also to the oxygen concurrently absorbed.

The tripositive manganese was produced by adding permanganate to a solution containing an excess of manganous ion, acid and fluoride ion, the latter keeping tripositive manganese in solution by forming a complex manganic fluoride anion. In this way, no manganese higher than the tripositive state was present when oxalate was added.'

TABLE II

THE COMPOSITION OF THE REACTING MIXTURES

Millimoles per liter of solution

Reacting mixture	$KMnO_4$	$K_2C_2O_4$	$MnSO_4$	$KHSO_4$	KF
2	0.76	60	10	150	101
13	.76	60	5	150	101
6	.76	60	20	150	101
14	.76	60	40	150	101
3	.38	60	10	150	101
4	.76	30	10	150	101

The Mechanism

In order to facilitate the subsequent correlation of experimental data, it was deemed advisable to suggest at this point the most probable mechanism of the participation of oxygen.

In the absence of oxygen, or under conditions under which oxygen does not participate, the manganic–oxalate reaction was found to be well represented by the following series of equations[1]

$$Mn^{+++} + 2C_2O_4^{--} = Mn(C_2O_4)_2^{-} \text{ (rapid, reversible)} \tag{1}$$
$$Mn^{+++} + C_2O_4^{--} = Mn^{++} + CO_2 + CO_2^{-} \text{ (measurable)} \tag{2}$$
$$Mn^{+++} + CO_2^{-} = Mn^{++} + CO_2 \text{ (rapid)} \tag{3}$$

In order to account for the participation of oxygen, the following additional equations are proposed

$$CO_2^{-} + O_2 = O_2CO_2^{-} \text{ (rapid, reversible)} \tag{4}$$
$$O_2CO_2^{-} + Mn^{++} + 2H^{+} = Mn^{+++} + CO_2 + H_2O_2 \text{ (measurable)} \tag{6}$$

The ion, CO_2^{-}, is an intermediate oxidation product of oxalate ion. Since it has an unpaired electron, it should have a tendency to unite with the molecule, O_2, also having unpaired electrons, to form an electron pair bond.[3] Thus a peroxide of carbon is formed, as is shown in equation (4).

The presence of hydrogen peroxide in the final resulting solutions in which oxygen had been present was shown by the very strongly yellow color imparted to titanic sulfate solutions. In the case of one experiment, 2a (Air), the resulting hydrogen peroxide was determined to be 0.33 millimole, by adding potassium iodide to the final colorless solutions and titrating the slowly liberated iodine with thiosulfate, the correction for the iodine liberated by oxygen being negligible. The amount of oxygen found to have been absorbed was 0.353 millimole. Resulting solutions in which no oxygen had been present gave no noticeable test for peroxides.

The appearance of hydrogen peroxide during the permanganate–oxalate titration was observed and studied by Schroder and most recently by Kolthoff,[4] among others, who ascribed its presence to the following reaction

$$O_2 + C_2O_4^{--} + 2H^{+} = H_2O_2 + 2CO_2 \tag{6}$$

It is to be noted that this equation (6) is the sum of equations 2, 4 and 5, above, and that these latter provide a mechanism for the net reaction (6). More exact proof of the stoichiometric correctness of this equation will be presented below.

Furthermore, it was most logical to assume that a carbon peroxide oxidizes the manganous ion, since neither gaseous oxygen nor hydrogen peroxide reacts with manganous ion under the conditions of these experiments.

The Regeneration of Manganic Ion

One explanation for the longer persistence of color due to tripositive manganese, when oxygen is present, is that a peroxide of carbon reacts

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(3) Launer, THIS JOURNAL, 54, 2597 (1932).

(4) Schroder, *Z. öffentl Chem.*, 16, 270 and 290 (1910); Kolthoff, *Z. anal. Chem.*, *64*, 183 (1924).

with manganous ion to produce manganic ion, presumably according to equation (5). If this is the case, an increase in the concentration of manganous ion should be accompanied by an increase in the rate of formation and amount formed of manganic ion, when oxygen is present, if reaction (5) is measurably slow. This in turn should result in an increase in the rate of formation and amount formed of carbon dioxide.

This was found experimentally to be the case. The curves 13ab (Air), 2a5 (Air), 6ab (Air) and 14ab (Air), Fig. 2, represent the rate of formation of carbon dioxide in experiments in which the amounts of manganous ion originally added varied as 1 : 2 : 4 : 8, respectively, as is shown in Table II. From the data inscribed in Fig. 2, it is seen that not only the rates of formation, but also the weights and final pressures of carbon dioxide varied as the manganous ion added, when oxygen was present.

When oxygen was absent, however, the evolution of carbon dioxide was absolutely independent of the concentration of manganous ion. This was determined by repeating experiment $2(N_2)$ except that four times as much manganous ion was added, this experiment thus being called $14(N_2)$. The rate measurements of $2(N_2)$ and $14(N_2)$ were found to be identical within 0.5 cm. of water, and the weights of carbon dioxide within 0.6 mg. Repetition of both experiments gave the same results, thus showing that the concentration of manganous ion is without effect when oxygen is absent.

The Factors Governing the Absorption of Oxygen

(1) The Partial Pressure of Oxygen.—A five-fold increase in the pressure of oxygen resulted in only a small increase in the rate of its absorption, as is seen from a comparison of the first parts of curves 2b (Air) and $2b(O_2)$, Fig. 1. This points to an equilibrium between the O_2 molecule and the ion CO_2^-, according to equation (4), above, the resulting peroxide of carbon being only slightly dissociated. Thus, a five-fold increase in the pressure of oxygen would increase but slightly the concentration of the peroxide of carbon, but would decrease five-fold the concentration of the ion CO_2^-. This in turn would decrease greatly the amount of CO_2^- oxidized per unit time by Mn^{+++} in reaction (3). Since reaction (3) prevents the process from continuing until the oxygen is exhausted, any decrease in the rate of reaction (3) must result in a longer continuation in the process, and hence a greater oxygen absorption. This greater oxygen absorption is seen from a comparison of the final pressures of 2b (Air) and 2b (O_2), shown in Fig. 1.

(2) The Concentration of Manganic Ion.—There was a considerable decrease in the rate of absorption and amount absorbed when the manganic ion concentration was decreased. This is seen from a comparison of the curves for experiments 2b (Air) and 3b (Air), Fig. 1, the concentration of manganic ion being in the ratio of 2:1, respectively.

(3) The Concentration of Manganous Ion.—The rate of absorption and the amount absorbed of oxygen was increased by increasing the manganous-ion concentration. This is seen from a comparison of the rate data for experiments 13b (Air), 2b (Air), 6b (Air) and 14b (Air) in Table III. The amounts of manganous ion added were in the ratios 1 : 2 : 4 : 8, respectively.

TABLE III

THE EFFECT OF MANGANOUS ION

13b (Air)		2b (Air)		6b (Air)		14b (Air)	
Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O
5	− 8.1	5	−10.5	5	−10.9	5	−10.5
10	−13.6	10	−17.2	10	−18.8	10	−19.0
15	−18.2	15	−22.7	15	−25.4	15	−26.4
20	−22.6	20	−27.9	20	−30.8	20	−32.7
30	−30.1	30	−36.7	30	−39.9	30	−43.2
40	−36.2	40	−43.7	40	−47.6	40	−51.8
50	−41.2	50	−49.6	50	−53.9	50	−58.7
60	−45.7	60	−54.9	60	−59.2	60	−64.4
∞	−69.1	110	−71.5	∞	−89.5	∞	−94.8
		∞	−83.3				

The more rapidly manganic ions are regenerated, the more rapidly the ion CO_2^- will arise as in reaction (2), above, and unite with oxygen. This reasoning is borne out by the fact shown above, that the rate of absorption and amount absorbed of oxygen was lowered by decreasing the manganic-ion concentration.

(4) The Concentration of Oxalate Ion.—A comparison between the curves for experiments 2b (Air) and 4b (Air) Fig. 1, shows that a decrease in the concentration of the oxalate ion resulted in a decrease in the rate of absorption and amount absorbed of oxygen. In view of the presence of fluoride ion, the prediction of the effect on the manganic ion concentration of changing that of the oxalate ion, is uncertain. The effect, however, of oxalate ion on the rate of absorption of oxygen is seen to be in agreement with the above mechanism.

TABLE IV

Expt.	Millimoles CO_2 from Henry's law constant	Millimoles CO_2 by analysis	Millimoles O_2 absorbed	Millimoles CO_2 in the N_2 experiments	Ratio, moles CO_2 to moles O_2
13 (Air)	0.99	1.05	0.292	(0.396)[a]	2.04
2 (Air)	1.06	1.11	.353	.396	1.89
6 (Air)	1.14	1.24	.379	(.396)	1.96
14 (Air)	1.23	1.30	.402	.384	2.10
2 (O_2)	1.55	1.70	.555	.396	2.07
4 (Air)	0.75	0 90	.184	(.396)	1.93
3 (Air)	0.80	0.89	.310	(.198)	1.94

[a] The values in parentheses were simply taken from experiment 2, since it was not thought necessary to carry out oxygen-free experiments in all cases.

The Relation between the Amount of Oxygen Absorbed and the Resulting Amount of Carbon Dioxide Evolved.—Equation (6), above, evidently requires that the ratio of the number of moles of carbon dioxide evolved in reaction 6 to the number of moles of oxygen absorbed be as 2 : 1. This is in harmony with experimental facts, as can be seen from the ratios, for the various experiments, given in the last column of Table IV.

For the purpose of obtaining the ratios in the last column, the moles of carbon dioxide calculated from the Henry's law constant were used,

TABLE V

THE RATE DATA

The data for the "ab" curves are not listed below, but may be calculated by combining the corresponding "a" and "b" data. The "b" data not appearing below may be found in Table III, above.

Expt. 2a (Air) Time, min.	Press., cm. H_2O	Expt. 2 (N_2) Time, min.	Press., cm. H_2O	Expt. 2a(O_2) Time, min.	Press., cm. Hz0	Expt. 2b (O_2) Time, min.	Press., cm. H_2O
5	8.9	5	15.7	5	6.3	5	−9.6
10	15.3	10	24.8	10	11.6	10	−18.1
15	20.6	15	30.5	15	16.8	15	−25.0
20	25.0	20	35.8	20	21.5	20	−31.2
30	32.7	30	40.7	30	29.8	30	−41.5
40	37.9	40	43.5	40	35.3	40	−50.0
50	41.8	50	45.3	50	39.9	50	−57.5
60	44.3	60	46.5	60	43.3	60	−64.6
70	46.6			70	46.0	70	−71.0
80	48.5			80	48.2	80	−76.4
90	50.1					110	−88.9
∞	53.9	∞	48.3	∞	71.3	∞	−130.8

3b (Air)		3a (Air)		4a (Air)		4b (Air)	
5	−6.5	5	4.4	5	15.8	5	−3.3
10	−11.6	10	6.6	10	25.6	10	−7.9
15	−16.4	15	8.6	15	32.8	15	−11.9
20	−20.4	20	10.6	20	37.4	20	−15.7
30	−27.2	30	14.3	30	43.2	30	−21.4
40	−32.8	40	17.3	40	46.6	40	−26.0
50	−37.8	50	19.8	50	48.3	50	−29.9
60	−42.6	60	22.0	60	49.1	60	−32.5
80	−49.7	80	25.5				
100	−55.5	100	27.8				
∞	−68.7	∞	35.5	∞	53.9	∞	−43.5

6a (Air)		13a (Air)		14a (Air)	
5	9.1	5	10.6	5	30.0
10	15.8	10	17.1	10	16.6
15	21.5	15	22.5	15	22.6
20	26.7	20	27.2	20	27.8
30	34.8	30	34.3	30	35.8
40	40.2	40	39.2	40	41.8
50	44.2	50	42.6	50	46.0
60	48.1	60	45.2	60	49.4
∞	58.3	∞	59.5	∞	65.2

diminished, of course, by the moles of carbon dioxide evolved in the absence of oxygen, in the N_2 experiments. This was considered more reliable than a calculation based upon the weights of carbon dioxide found by analysis, since it was found that during the time of sweeping out the carbon dioxide at the end of the experiments in which oxygen had been present, some carbon dioxide was always produced, accompanied by absorption of oxygen. This did not occur in the experiments in which oxygen had been absent, although they too were swept out with air. This seems to indicate that the ion CO_2^- or the peroxide of carbon was still present at the "end" of the reaction. The number of moles of oxygen absorbed was calculated from the final pressures in the corresponding "b" experiments, the volume of the gas space, the solubility of oxygen in water, and the temperature, using the relation $pv = NRT$.

Summary

It was found that when the reaction between manganic ions and oxalate ions took place under certain conditions, the color, due to tripositive manganese, persisted much longer when oxygen was present than when the latter was absent. This was shown to be due, most probably, to a regeneration of the manganic ion in a reaction between manganous ions and a peroxide of carbon.

It was further found that large quantities of oxygen were absorbed during the manganic-oxalate reaction, under certain conditions, and the rate of this absorption was studied in detail. As a consequence of this absorption of oxygen, proportional quantities of carbon dioxide, in addition to the carbon dioxide expected from the manganic–oxalate reaction, were evolved, the ratios being 2 moles of CO_2/1 mole of O_2.

It was, therefore, suggested that the mechanism of the participation of oxygen be described by the chemical equations

$$O_2 + CO_2^- = O_2CO_2^-$$
$$O_2CO_2^- + Mn^{++} + 2H^+ = Mn^{+++} + CO_2 + H_2O_2$$

Hydrogen peroxide was always found in the resulting solutions in which oxygen had been present, but never in those in which the latter had been absent.

LOS ANGELES, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Ternary Systems: Water, Tertiary Butanol and Salts at 25°

BY P. M. GINNINGS, ETHEL HERRING AND BAILEY WEBB

Results of an investigation of this group of systems were published in a paper[1] but it was not until later[2] that the idea occurred to investigate the mathematical aspects of these systems. In the latter paper the concentration of the isopropanol as a function of the concentration of the salt was investigated and it seemed desirable to supplement the work on tertiary butanol by an analogous investigation. This has been done with thirty diversified salts in their thirty ternary systems. The purpose of the unusual number of systems was to render improbable any coincidental relationships which might occur if only a few systems were investigated. Tertiary butanol is especially suitable here on account of the ease with which it is salted out from its homogeneous aqueous solutions by a large number of salts.

In the preliminary work, a temperature of 30° was used, the idea being that the higher temperature would be above the critical temperatures for some systems. However, the necessity for increased accuracy in the experimental data made it imperative that the room temperature be maintained constant also. Everything considered, 25° seemed to be the optimum temperature and was used in preference to the 30°. The thirty systems investigated here at 25° include the ten systems previously reported upon at 30°.

The primary purpose was to ascertain what mathematical relationships, if any, could be found between the components of the systems. The concentration of the tertiary butanol as a function of the concentration of the salt seemed of greatest interest and received most attention. Experimental points of the binodal curves were first determined and the weight per cent. of tertiary butanol plotted as a function of the weight per cent. of the salt. Then the empirical mathematical equations were derived which seemed to approximate the experimental data the best. Because of a few coincidences at first, the tentative assumption was made that the two mathematical equations would always intersect in the plait point, but later results on other systems showed conclusively that this was not necessarily true in all systems. Consequently, the binodal curves were divided into two sections, the alcohol-rich section and the salt-rich section. Examination of the empirical equations which fit the alcohol-rich sections revealed that all thirty systems followed the exponential equation, $y = a + b(10)^{-cx}$ (y is weight per cent. of tertiary butanol and x the weight per cent. salt; a, b and c are arbitrary constants). From this can be derived the differential equation $-\mathrm{d}(y - a)/\mathrm{d}x = ky$. In one-half of the systems,

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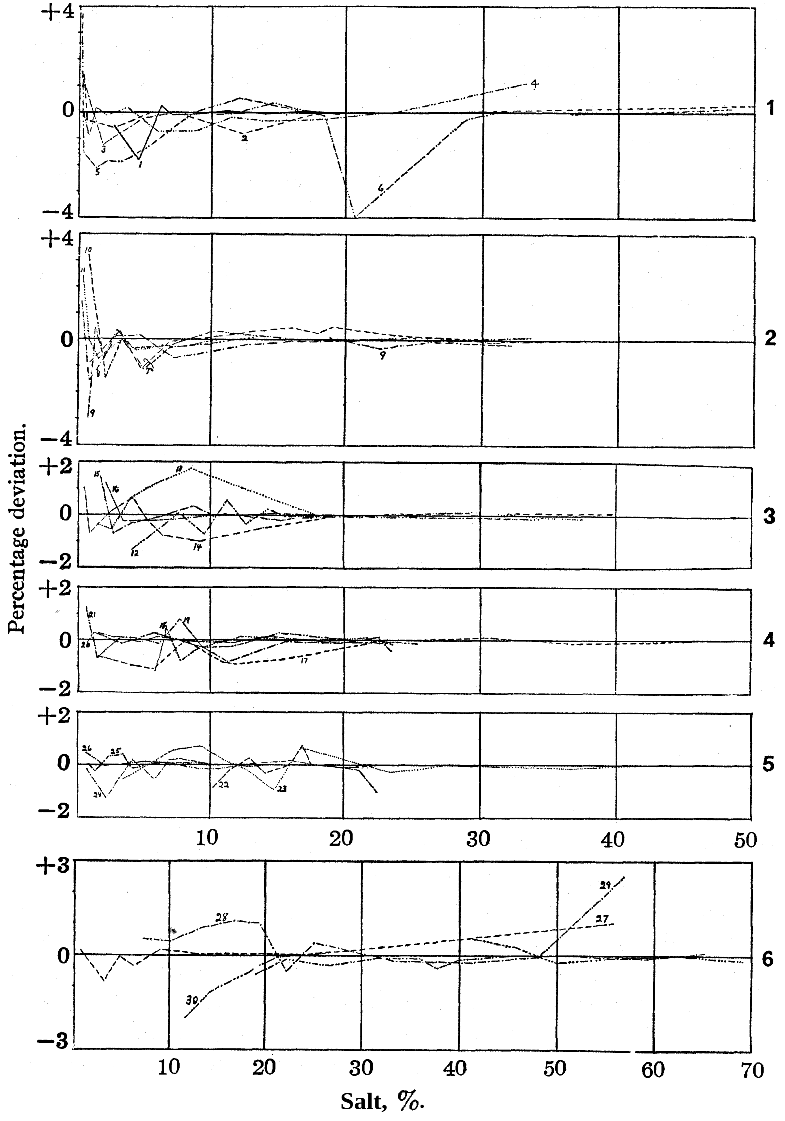
(1) Ginnings and Robbins, THIS JOURNAL, **52**, 2282–2286 (1930).

(2) Ginnings and Chen, *ibid.*, **83**, 3765–3769 (1931).

constant "*a*" approaches zero with the resulting simplification of the two equations. Of lesser importance but of some interest are the constants in the equations for the potassium halides. Constant "*b*" is a direct function



Deviation charts of experimental values of weight % of tertiary butyl alcohol from values calculated using the empirical equations.

and "*c*" an inverse function of the molecular weight of the halide. The case of the salt-rich sections of the binodal curves is not so distinct. Eighteen systems followed the above-mentioned exponential law and the other twelve seemed to he power functions of the type form $y = a + bx^{-c}$. No important relationship in this section was obvious although the exponential equation was evidently the one favored. Apparently, the salt component predominates here to such an extent that each system is primarily a function of the specific salt used.

Experimental

The experimental method was essentially identical with that used before[3] with minor improvements tending toward greater precision. The synthetical method was used to determine the plait point and seemed to be distinctly superior to the analytical method. In some cases interpolation between two binodal points to find the plait point was more convenient. This was done on the curve obtained by plotting the volume per cent. of one

TABLE I

(A) $y = a + b(10)^{-cx}$ (B) $y = a + bx^{-c}$

y = wt. % of *tert*-butanol; x = wt. % of salt; a, b, c are numerical constants

Dev. curve no.	Salt	Alcohol-rich section Eq.	a	b	c	Limit for x	Salt-rich section Eq.	a	b	c
1	NH_4Cl	A	0	117.4	0.0748	9.7	B	0	325	1.189
2	KF	A	0	71.7	.1330	5.0	A -	0	30.3	0.0583
3	$(NH_4)_2HPO_4$	A	5.9	59.25	.0835	16.1	A	−0.67	33.1	.0328
28	NH_4NO_3	A	0	121.6	,0266	21.6	B	−1.65	17458	2.016
29	KI	A	−44.9	158.3	.00969	38.4	A	−13.0	277.0	0.0233
19	KCl	A	14.2	74.4	.0992	5.4	B	0	331	1.326
4	$CdSO_4$	A	30.64	33.1	.2867	4.5	B	−34.0	112.2	0.3320
20	$K_3Fe(CN)_6$	A	33.9	38.8	.2185	4.3	B	−3.5	125.8	.7635
12	KBr	A	0	99.5	,0391	11.5	B	0	2690	1.750
30	KSCN	A	−44.5	164.7	.0109	37.9	A	0.63	4840	0.0624
10	Na acetate	A	0	89.1	.0787	4.7	B	0	269	1.215
14	$NaAl(SO_4)_2$	A	21.2	36.55	.1503	5.4	A	0	46.4	0.0440
11	Na_2SO_4	A	0	60.7	.0987	5.6	A	−22	51.2	.0209
5	$Na_2S_2O_3$	A	4.57	62.2	,0955	18.4	A	0	50.0	.0513
8	$ZnSO_4$	A	21.55	36.35	,1610	6.0	A	0	45.9	.0441
17	NaBr	A	0	101.8	.0403	11.0	B	−1.47	2175	1.682
9	$NaKCO_3$	A	0	68.1	.1284	4.0	A	0	37.1	0.0621
26	$(NH_4)_2SO_4$	A	2.95	63.05	,0909	8.3	A	0	30.46	.0405
18	$BaCl_2$	A	0	95.5	.0617	11.6	A	0	47.6	.0358
24	NaCl	A	0	88.5	.1030	6.6	B	0	214.6	1.298
16	$NaHSO_4$	A	0	61.1	.0518	8.0	B	−3.9	240.3	1.020
23	$NaNO_3$	A	0	93.5	.0399	11.6	B	−2.63	1523	1.640
22	$LiNO_3$	A	−75	218.5	.0218	16.0	A	3.88	1505	0.1186
13	KNa tartrate	A	3.70	59.8	.0849	11.0	A	−0.455	30.2	.0326
6	$SrBr_2$	A	30.75	323.3	.1030	20.7	B	−1.095	$1.986(10)^5$	2.845
7	$SrCl_2$	A	0	87.2	.0669	10.7	A	0	45.5	0.0398
27	K_2CO_3	A	0	63.1	.1014	6.9	A	−0.87	26.90	.0441
21	$MgSO_4$	A	5.50	45.75	.0988	8.0	A	0	34.65	.0530
25	Na_2CO_3	A	5.48	57.42	,1759	4.1	A	0	32.04	.0700
15	Natartrate	A	0	58.6	.0710	7.8	A	0.805	33.87	.0432

The empirical equation for the alcohol-rich section of the binodal curve of any specific system is valid for the interval between the smallest value of "x" in Dev. Ch. to the value in the column headed "limit for x" in Table I. Similarly, the empirical equation for the salt-rich section covers the interval between value for "x" in the column "limit **for** x" to the largest value in the deviation chart.

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(3) Ref. 2, p. 3767.

liquid phase as a function of the weight per cent. of salt. Interpolation to the *50%* intersection gave the desired plait point. The highest weight per cent. salt in a system in a Chart is approximately conjugate with the highest weight per cent. of tertiary butanol; and the lowest weight per cent. salt is conjugate with the lowest weight per cent. of tertiary butanol. Eastman's best grade of tertiary butanol, d_4^{20} *0.7872,* and C. P. chemicals were used throughout. Whenever hydrates of salts were used, the calculations were corrected to the basis of anhydrous salts. The authors feel that the error in binodal data does not exceed 1.0% in any case and is usually less than 0.5%.

TABLE II

PLAIT POINTS

Salt	Wt. % *t*-BuOH	Wt. % salt	Salt	Wt. % *t*-BuOH	Wt. % salt
NH_4Cl	37.6	6.6	KF	36.3	2.2
$(NH_4)_2HPO_4$	33.8	3.8	NH_4NO_3	33.1	21.6
KI	22.2	38.4	KCl	41.0	4.5
$CdSO_4$	21.3	8.1	$K_3Fe(CN)_6$	38.0	4.3
KBr	35.1	11.5	KSCN	19.3	37.9
Na acetate	38.0	4.7	$NaAl(SO_4)_2$	26.9	5.4
Na_2SO_4	31.4	2.8	$Na_2S_2O_3$	33.6	3.2
$ZnSO_4$	25.5	6.0	NaBr	36.3	11.0
$NaKCO_3$	31.6	2.6	$(NH_4)_2SO_4$	35.4	3.2
$BaCl_2$	34.1	7.2	NaCl	36.7	3.7
$NaHSO_4$	29.5	6.1	$NaNO_3$	32.4	11.6
$LiNO_3$	23.0	16.0	KNa tartrate	31.1	4.0
$SrBr_2$	29.8	20.4	$SrCl_2$	33.1	6.3
K_2CO_3	36.3	2.3	$MgSO_4$	27.2	3.3
Na_2CO_3	32.2	2.1	Na tartrate	31.4	3.8

Summary

Data are given for the ternary systems of water and tertiary butanol with thirty salts at 25°. In the case of the alcohol-rich section of the binodal curves for the thirty systems, the rate of decrease of the weight per cent. of the tertiary butanol with respect to the weight per cent. of salt in a liquid phase seems to be a direct function of the weight per cent. of tertiary butanol. The constants in the equations for the four potassium halides are compared. Values for the numerical constants in the empirical equations and deviation charts are given for all of the systems.

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Solubility Relations of Barium Sulfate in Aqueous Solutions of Strong Electrolytes

BY EDWARD W. NEUMAN[1]

In two preceding articles[2],% method for the determination of the solubility of slightly soluble inorganic salts in aqueous solutions of strong electrolytes was described and applied to a uni-univalent salt, silver chloride. In the second paper the data were discussed from the viewpoint of the recent developments in the interionic attraction theory of solutions of Debye and Hückel[4] as presented by Gronwall, La Mer and Sandved[6] and by La Mer, Gronwall and Greiff.[6]

In the present paper the same experimental method and treatment of the data have been applied to a di-divalent type salt, barium sulfate, in an attempt further to test the extension of the theory.

Experimental

The technique, applicability and limitations of the experimental method have already been described and discussed in detail. Materials used in the preparation of solutions were all carefully purified and tested. Water was twice distilled. The second time it was done through a block tin condenser. The maximum conductivity of several samples was 1.2 × 10^{-6} mho. Water and solutions were prepared in small quantities so as to minimize the effects of solubility of glass. The effect of carbonic acid in the water in equilibrium with carbon dioxide in the air will be described later. Experiments were made showing that the same results obtained whether equilibrium was attained from the solid or from the liquid phase.

Data and Discussion

The solubility of barium sulfate was measured at 25° in the presence of the chlorides and the nitrates of potassium, magnesium and lanthanum up to an ionic strength of about 0.04.

The value of the solubility, S_0, in otherwise pure water was determined statistically from the data on each solvent salt by applying the method of moments and the relation

$$S = S_0 + A\mu^{1/2} \qquad (1)$$

to the five lowest points where a straight line relationship may be considered sufficient. Here S is the observed solubility at a given molality of the solvent salt which is expressed in terms of the ionic strength μ, and A is a con-

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(1) National Research Fellow in Chemistry.

(2) Popoff and Neuman, *J. Phys. Chem.*, 34, 1853 (1930).

(3) Neuman, THIS JOURNAL, **54**, 2195 (1932).

(4) Debye and Hückel, *Physik. Z.*, 24, 185 (1923).

(5) Gronwall, La Mer and Sandved, *ibid.*, 29, 358 (1928).

(6) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

stant. An extrapolation for S_0 is necessary because the experimental method does not permit a direct measurement. The value of $\log f_0$, where f_0 is the activity coefficient corresponding to S_0, was evaluated similarly, with the use of the formula

$$\log (S/S_0) = \log f_0 + b\mu^{1/2} \qquad (2)$$

where b is a constant, and μ is the ionic strength. Here μ contains, in addition, the concentration of the solute salt.

The ionic strength of all of the solutions contains a correction which accounts for ionized carbonic acid in the water in equilibrium with the carbon dioxide of the air. This correction amounts to 0.615×10^{-5} μ, and it is an average value calculated from the work of Kendall for equilibrium water.[7] This correction becomes negligible above 0.01 μ, but it amounts to about 6% of the ionic strength at 0.0001 μ. When the correction is not made, S_0 becomes 0.3%, and f_0 about 0.2% greater. These differences, however, are less than the experimental error which is due to measuring of solutions and to error in the tyndallometric readings involved in fixing the end-points. Moreover, it should be noted also that the theoretical results, and all comparisons with theory, depend only on the precision of relative values produced by salt additions so that a slight error in absolute value does not obviate comparison with the theory.

The results of the statistical treatment of the lowest points are given in Table I. The mean deviation in S_0 is 0.01 X 10^{-6}, or about 1%; that info, about 0.002 or 0.2%. The values f in the third column represent the slope from the data on each solvent salt, and if the limiting law were obeyed in each case they should equal 2.026, the value α in the Debye–Hückel formula for a (2, −2) valence type solute salt. The deviations from the limiting law as expressed by the ratio b/α increase with greater complexity of the solvent salt in the order (3, −1) > (2, −1) > (1, −1); that is, for a given ionic strength and anion, the solution effect of the various cations is in the order $La^{+++} > Mg^{++} > K^+$. These ratios indicate also that for a given cation, nitrates increase the solubility more than do chlorides. This

TABLE I

EMPIRICAL PARAMETERS FROM STATISTICAL TREATMENT OF DATA

Salt	S_0 X 10^6	$-\log f_0$	b	b/α	f_0
KCl	0.970	0.00891	2.592	1.28	0.980
KNO_3	.971	.00960	2.624	1.30	.978
$MgCl_2$	.955	.01053	3.064	1.51	.976
$Mg(NO_3)_2$	.961	.01061	3.095	1.53	.976
$LaCl_3$	.947	.01085	3.592	1.77	.975
$La(NO_3)_3$	.938	.01096	3.706	1.83	.975
Mean Cl^-	.957	.01011	...	..	.977
Mean NO_3^-	.957	.01040	...		.976
Average	.957	.01026		..	.977
Not corr. for H_2CO_3	.960	.00938		..	.979

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(7) Kendall, THIS JOURNAL, 38, 1480 (1916).

effect, however, is very slight; and were it not for the consistency with which it appears in all of the cases noted it might be attributed to experimental error. Values of S_0, f_0 and $-\log f_0$, calculated without the correction for carbonic acid, appear at the bottom of the table.

The experimental data appear in Table II. The average values, $S_0 = 0.957 \times 10^{-5}$ m./l. and $\log f_0 = -0{,}01026$, were used throughout for the calculation of log f by means of the relation

$$-\log f = \log (S/S_0f_0) \tag{3}$$

TABLE 11

SOLUBILITY RELATIONS OF BARIUM SULFATE

$S \times 10^5$	$M_{\text{Solvent Salt}}$	$\mu^{1/2}$	$-\log f_{\text{(obs.)}}$	$-A$	$-a[1]$	$a[5]$
			Solutions of Potassium Chloride			
1.002	0.00002004	0.00814	0.0303	0.0138	162	
1.067	.0002631	.01762	.0575	.0218	65 5	
1.123	,0006477	.02643	.0798	.0262	37.8	2 30
1.193	.001361	.03763	.1070	0308	23.3	2 60
1.274	.002526	.05082	.1345	0316	14.1	2 90
1.354	003875	06273	.1620	.0348	10.4	2 98
1.445	.005631	.07546	.1892	0363	7 73	3 13
1.532	.007611	.08763	.2150	.0374	6 04	3 05
1.615	.009974	.10022	.2375	.0345	4.41	3 34
1.715	.01263	.1167	.2636	.0372	1.95	3.50
1.797	.01543	.1249	.2839	0308	2.48	3 35
1.885	.01885	.1375	.3047	.0261	1.90	3 38
1.975	,02141	.1466	.3249	.0279	1.78	3.39
2.090	.02631	.1624	.3495	0204	1.09	3 36
2 195	.03053	.1750	.3708	.0162	0.759	3 35
2.320	,03501	.1874	.3949	.0151	0.621	3 28
			Solutions of Potassium Nitrate			
1.007	0.00002014	0.00816	0.0324	0.0159	183	
1.085	.0003566	.02015	.0648	.0240	55.9	
1.143	.0008528	.03008	.0874	.0242	28.0	2.59
1 213	.001554	.04011	.1132	,0299	20.0	2.67
1.277	.002456	.05013	.1356	.0340	15 2	2.86
1.412	.004848	.07008	.1792	0371	8 99	3 05
1.565	.008031	.09000	.2239	.0415	6.27	3 08
1.695	.01203	.11002	.2585	.0356	3.81	3 10
1.855	.01684	.1300	.2977	.0342	2.68	3.26
2.010	.02252	.1503	.3326	.0279	1.70	3.27
2.185	.02884	.1699	3688	.0245	1.19	3.25
2.355	03602	.1899	.4014	.0166	0.662	3.26
			Solutions of Magnesium Chloride			
						$a[3]$
1.002	0.00001002	0.00874	0.0302	0.0125	144	
1.085	.0001198	.02027	.0648	.0238	55.3	
1.167	.0002856	.03016	0964	.0353	36 9	
1.240	.0005173	.04009	.1228	.0416	25.7	0 43

TABLE II (*Concluded*)

$S \times 10^5$	$M_{\text{Solvent Salt}}$	$\mu^{1/2}$	$-\log f_{(\text{obs.})}$	$-$ A	$-a_{[1]}$	$a_{[3]}$
1.309	0.0008120	0.04984	0.1463	0.0453	18.9	0.64
1.388	.001179	.05997	.1718	.0502	14.8	.90
1.547	.002113	.08003	.2189	.0567	9.85	1.16
1.705	.003227	.09876	.2611	.0610	7.20	1.38
1.845	.004773	.1200	.2957	.0522	4.49	1.64
2.015	.006410	.1390	.3337	.0520	3.41	1.76
2.185	.008512	.1601	.3688	.0444	2.29	1.87
2.340	.01064	.1790	.4001	.0373	1.58	1.96
Solutions of Magnesium Nitrate						
1.007	0.00001007	0.00875	0.0324	0.0147	158	
1.098	.0001199	.02027	.0700	.0289	62.0	
1.172	.0002856	.03016	.0983	.0371	38.1	
1.253	.0005174	.04011	.1273	.0460	27.4	0.40
1.322	.0008151	.05004	.1506	0492	19.9	.54
1.474	.001609	.06994	1979	0561	12.3	.99
1.633	.002686	.09016	2424	.0597	8.31	1.33
1.784	.004008	.1100	.2808	.0579	5.70	1.56
1.935	.005699	.1299	.3161	.0528	3.91	1.73
2.110	.007461	.1499	.3537	.0499	2.86	1.80
2.285	.009593	.1700	.3883	.0438	2.01	1.90
2.458	.01199	.1897	.4200	.0351	1.34	1.97
Solutions of Lanthanum Chloride						
1.007	0.00000668	0.00930	0.0324	0.0136	137	
1.113	.00005571	.01962	.0759	.0361	73.7	2.11
1.194	.0001550	.03137	.1064	.0428	39.0	2.78
1.285	.0002543	.03851	.1383	.0602	34.3	2.83
1.375	.0004026	.04977	.1677	.0668	24.4	3.32
1.468	.0005849	.05979	.1961	.0749	19.4	3.63
1.695	.001070	.08059	.2585	.0952	13.9	3.92
1.832	.001667	.10041	.2923	.0888	9.20	4.39
2.014	.002400	.1204	.3334	.0896	6.79	4.53
2.208	.003353	.1421	.3734	.0855	4.90	4.58
2.394	.004296	.1609	.4085	.0825	3.82	4.62
Solutions of Lanthanum Nitrate						
1.003	0.00000667	0.00930	0.0307	0.0120	128	
1.112	.00005923	.02017	.0755	.0346	69.1	1.40
1.182	.0001447	.03037	.1020	.0404	39.6	2.62
1.290	.0002599	.04022	.1398	.0583	31.5	2.92
1.390	.0004102	.05022	.1733	.0716	25.0	3.29
1.485	.0005924	.06016	.2011	.0792	19.9	3.55
1.573	.0008107	.07023	.2261	.0838	16.1	3.83
1.664	.001071	.08061	.2525	.0892	13.3	4.04
1.845	.001652	.09996	.2954	.0928	9.56	4.28
2.037	.002374	.1197	.3384	.0958	7.20	4.37
2.223	.003315	.1414	.3763	.0871	4.98	4.48
2.405	.004276	.1605	.4105	.0853	3.94	4.55

The values A represent deviations from the Debye-Hückel limiting law obtained from

$$
\begin{aligned}
A &= 2.0262\,\mu^{1/2} - \log f \\
&= \log f_{[1]} - \log f_{(\text{obs.})} \qquad (4)
\end{aligned}
$$

The maximum deviations from the limiting law, in the range studied, occur at about 0.0077 μ for the potassium salts, 0.0090 μ for the magnesium salts and 0.011 μ for the lanthanum salts.

The apparent ionic diameters, $a_{[1]}$, are the parameters necessary to make log $f_{[1]}$ of the Debye–Hückel first approximation formula coincide with log $f_{(\text{obs.})}$. They are evaluated from the relation

$$a_{[1]} = -\Delta/0.3287\,\mu^{1/2}\log f_{(\text{obs.})} \qquad (5)$$

which is derived from the first approximation formula. The apparent ionic diameters, $a_{[3]}$, are similarly derived from the third approximation formula of La Mer, Gronwall and Greiff[6] for unsymmetrical valence type electrolytes; and the $a_{[5]}$ values are derived from the formula of Gronwall, La Mer and Sandved[5] for symmetrical valence type electrolytes. All of the a values are given in Ångström units in the tables.

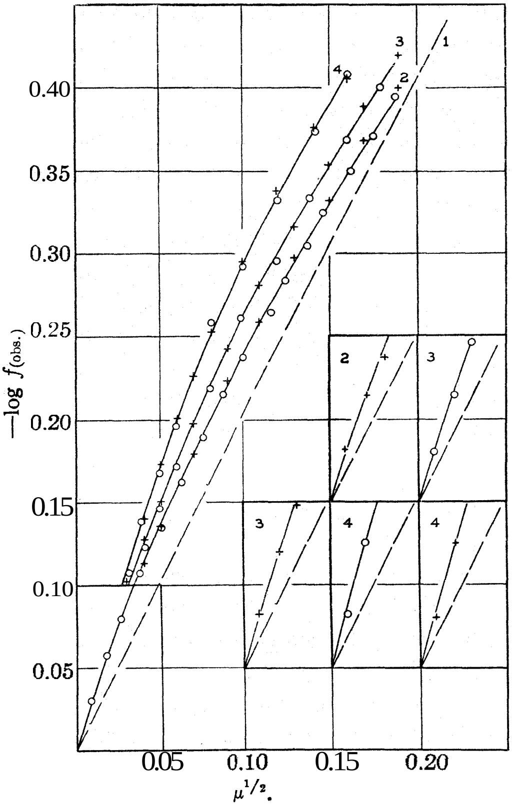

Fig. 1.—The logarithm of the observed activity coefficient as a function of the square root of the ionic strength: circles, chlorides; crosses, nitrates. 1, Debye–Hückel limiting law; 2, potassium salts; 3, magnesium salts; 4, lanthanum salts. The small figures are the portions of the curves between the 0 and 0.05 abscissas and the 0 and 0.1 ordinates.

From a consideration of the deviations A, and the a values, it is apparent that neither the limiting law nor the first approximation formula is in accord with the data. The $a_{[1]}$ values are both inconstant and negative, thereby contradicting the theory. There is a more exact agreement with the extended formulas of La Mer and of Gronwall, as is indicated by the $a_{[3]}$ and the $a_{[5]}$ values, which are more nearly constant and positive; and they are of reasonable magnitude. The agreement in the case of the fifth approximation for symmetrical valence types is especially striking, chiefly at the greater ionic strengths.

The $a_{[3]}$ and $a_{[5]}$ values which were omitted from the tables were only approximated. They were positive, but they became very small for the very low ionic strength. It is here that the theoretical curves for log f begin to converge into the limiting law, which is not the case with the data. Consequently, also, small errors in log $f_{(\text{obs.})}$, in this region, are greatly magnified in the resulting a values, whether they are derived from the first approximation formula or from the extended forms, and the a values, therefore, lose much of their value as a means of comparison of experiment and theory. Furthermore, their calculation is greatly complicated by increasing difficulty in accurate interpolation on curves of functions required in their computation. Because of these considerations they were omitted entirely from the tables.

In Fig. 1 the values of $-\log f_{(\text{obs.})}$ are plotted against the square root of the ionic strength. The lower portions of the curves, between 0 and 0.05 $\mu^{1/2}$, are plotted separately to avoid confusion of points which belong to the various solvent salts. The broken line represents the slope of the limiting law. The heavy lines are drawn only through the chloride points which are represented by circles. The nitrate points are designated by crosses.

Summary

The solubility of barium sulfate was determined in water at 25° in the presence of the chlorides, and the nitrates of potassium, magnesium and lanthanum over a concentration range, 0 to 0.04 ionic strength.

The solubility, and the activity coefficient of the salt in pure water, were evaluated statistically and found to be 0.957 X 10^{-5} m./l., and 0.977, respectively.

The activity coefficients, and the apparent ionic diameters, were calculated, and were used as a means of comparison of the data with recent developments in the interionic attraction theory of solutions.

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The Thermochemical Constants of the Hexafluorides of Sulfur, Selenium and Tellurium

BY DON M. YOST AND WILLIAM H. CLAUSSEN

Introduction

The hexafluorides of the elements of the sulfur group are of interest because of the uniformity of their physical properties, their comparative unreactivity, and the fact that in these compounds sulfur, selenium and tellurium exhibit their maximum valence of six. All three substances are gases at ordinary temperatures, they sublime before melting, and, with the exception of tellurium hexafluoride, they do not hydrolyze in the presence of water.

Aside from the earlier work of Moissan[1] and of Prideaux,[2] no further investigations of the hexafluorides of selenium and tellurium appear to have been carried out, and in their investigations no careful attempt was made to purify the substances prepared. Schumb and Gamble[3] have carried out a careful study of the preparation and physical properties of sulfur hexafluoride and their results are presented below for purposes of comparison. No determinations of the heats of formation of any of these three compounds seem to have been made.

In addition to the hexafluorides small quantities of liquid lower fluorides are formed when fluorine reacts with the elements of the sulfur group and, with the exception of sulfur tetrafluoride,[4] these substances have not previously been observed.

In this article are presented the results of experiments on the preparation and physical and chemical properties of selenium and tellurium hexafluorides and the values obtained for the heats of formation of sulfur, selenium and tellurium hexafluorides. Results of experiments on a lower fluoride of tellurium are also included.

Preparation and Purification of the Hexafluorides.—The hexafluorides were prepared by passing fluorine gas from a generator over the elementary substances contained in a copper tube. The reaction in all cases took place without any major disturbances such as explosions or extensive attack on the copper container. The fluorine was generated at the rate of about one and one-half liters per hour, the generator being of the conventional type using fused potassium acid fluoride as the electrolyte. The current efficiency was about 30%. The substances prepared were collected in *Pyrex* glass traps cooled with a carbon dioxide–alcohol

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(1) Moissan, Ann. *chim. phys.*, [7] **27**, 145 (1902).

(2) Prideaux, J. *Chem. Soc.*, 89, 323 (1905).

(3) Schumb and Gamble, THIS JOURNAL, 62,4302 (1930).

(4) Fischer and Jaenckner, *Z. angew. Chem.*, **42**, 810 (1929).

mixture. Hydrogen fluoride was effectively removed by causing the gas from the generator to pass through a copper tube containing anhydrous sodium fluoride.

The resulting material was purified by means of a series of fractional sublimations carried out in highly evacuated containers, liquid air being used to remove the more volatile products, and alcohol cooled with carbon dioxide served to fractionate what remained. The substances were caused to melt between the sublimation operations. Very little highly volatile product was obtained and only in the case of tellurium were appreciable quantities of a much less volatile substance found. The test for purity was the constancy of the freezing point and the vapor density of the substance being purified.

Experimental Methods

The vapor densities were determined by means of a liter flask equipped with an all-glass click-gage for measuring the pressure, and a standardized thermometer graduated in tenths of a degree served for the temperature measurements.

The apparatus used for the vapor pressure measurements consisted of an all-glass click-gage to which a glass container was attached by means of small-bore tubing. The container was surrounded by a well stirred alcohol-bath cooled with carbon dioxide or liquid air, and the click-gage was outside of this bath with its temperature that of the room. The bath temperature was measured with a thermocouple calibrated at the solid carbon dioxide and melting mercury points. No pressure measurements were made until variations of the temperature by ±0.1° caused a corresponding change in the pressure.

All melting points were determined separately and are believed to be correct to within ±0.1°.

The calorimeter for determining the heats of formation of the three hexafluorides consisted of a two-liter Dewar flask surrounded by a thick layer of insulating material and equipped with a tight insulating cover. It was provided with an electrically operated stirrer, an electric heating coil for determining its heat capacity and a Beckmann thermometer, and contained from 1.2 to 1.4 liters of distilled water. A hollow cylindrical copper tube 2.5 cm. in diameter and length and provided with a threaded copper plug was employed as a reaction cell. A rubber gasket rendered the threaded joint water and gas tight and the threads, after screwing the plug firmly into the cell, prevented any appreciable diffusion of the fluorine to the gasket. Two small copper tubes attached to the cell and passing through the cover of the calorimeter were used for introducing the fluorine and removing the hexafluoride formed, the exhaust tube being coiled near the reaction cell to facilitate complete heat transfer.

A deep platinum dish placed in the reaction cell was used to hold the solid reactants, and it was found that neither the fluorine nor the sulfur group elements had any appreciable effect on the platinum. A copper dish was used in some preliminary experiments but it was found to be attacked by sulfur during the course of the reaction with fluorine. The only losses of solid material were the result of vaporization to the copper walls of the cell and were estimated qualitatively as a few tenths of a milligram. The weights of material used in the runs varied from 0.2000 g. to 0.4000 g. and the temperature rise varied from about 0.750 to 1.100". A satisfactory run occupied about fifteen minutes and the same length of time was employed in determining the heat capacity of the calorimeter. Blank runs made with no reactant in the cell showed that no appreciable amount of reaction took place between the fluorine and the copper.

The errors involved in the vapor pressure measurements vary from ±0.2 mm. at the lowest pressures to ±2.0 mm. at the highest. The individual values for the heats of reaction showed deviations from the mean of 1.5% in the case of sulfur, 0.7% for selenium and 0.3% for tellurium. It is believed that the final results given are reliable to within 2%. More refined measurements will certainly necessitate the use of an all-platinum reaction cell to reduce to a minimum the errors due to the small losses by evaporation to the walls of the cell. The eventual loss in heat liberated appears to be due to the unreactivity of the fluorine toward the copper sulfide formed.

Results of the Experiments

In Tables I and II are presented the results of the vapor pressure and vapor density measurements.[5] The vapor pressure equations constructed from the experimental data are given in Table III. Table IV contains the thermochemical constants for the three hexafluorides as determined directly or calculated from the vapor pressure measurements. The values given

TABLE I

THE VAPOR PRESSURES OF SOLID SeF_6

Temp., °C.	Pressure, mm.
−48.7	651.2
53.8	469.3
59.4	318.4
64.8	213.1
69.3	147.9
77.9	72.1
84.4	43.3
87.5	30.4

Molecular wt., exptl., 191.3
Formula wt., calcd., 193.0

TABLE II

THE VAPOR PRESSURES OF SOLID TeF_6

Temp., °C.	Pressure, mm.
−40.1	695.1
45.6	501.6
50.0	361.3
56.7	246.6
60.3	182.5
65.3	122.2
68.4	94.1
74 7	53.4
75 4	48.4
78 8	29.4

Molecular wt., exptl., 240.9
Formula wt., calcd., 241.5

TABLE III

VAPOR PRESSURE EQUATIONS OF SOLID SULFUR, SELENIUM AND TELLURIUM HEXAFLUORIDES

$$SF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1231.3/T) + 8.7648$$

$$SeF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1440.8/T) + 9.2417$$

$$TeF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1471.4/T) + 9.1605$$

TABLE IV

THERMOCHEMICAL CONSTANTS OF THE HEXAFLUORIDES OF SULFUR, SELENIUM AND TELLURIUM

Subs.	Heat of formation of gas, cal.	Heat of sublimation of solid, cal.	Heat of fusion of solid, cal.	M. p., °C.	Sublimation point, °C.
SF_6	262,000	5640	1390	−50.8	−63.8
SeF_6	246,000	6600	(2010)	−34.6	−46.6
TeF_6	315,000	6740	(1900)	−37.8	−38.9

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(5) The recently published values for the vapor pressures of selenium and tellurium hexafluoride by Klemm and Henkel [*Z. anorg. allgem. Chem.*, *207*, 73 (1932)] are, at the lower temperatures, higher than those presented here. The difference appears to result from the fouling of the mercury in their manometer, and they call attention to this difficulty. This source of error has been avoided in our measurements by the use of the all-glass click-gage.

for sulfur hexafluoride, with the exception of its heat of formation, were obtained using the data of Schumb and Gamble.[3]

The values for the heats of fusion of selenium and tellurium hexafluorides, given in parentheses, were calculated from the heats of vaporization of the liquids which were obtained by an application of Trouton's rule to estimates of the boiling points using the known values for sulfur hexafluoride to determine the necessary constant. Since the melting point of tellurium hexafluoride is only *1.1'* above the sublimation point, the value for the heat of fusion cannot be in error by much more than *10* cal. The corresponding value for selenium hexafluoride may be in error by *50* cal.

All three hexafluorides have a vapor pressure of one atmosphere before the melting point is reached. The solid selenium hexafluoride, when condensed at the temperature of solid carbon dioxide–alcohol mixtures, forms a clear ice-like solid while the corresponding tellurium compound forms a white mass of small crystals.

A second modification of the tellurium compound appears to form at **−73.5'** since at this point a discontinuity in the log p–$1/T$ curve is observed.

The values obtained for the melting points differ appreciably from those obtained by Prideaux. The same lack of agreement was found by Schumb and Gamble in the case of the sulfur compound and is discussed more fully in their paper. Both lack of purity and the thermometer used are the obvious reasons for the differences.

Discussion of the Results

As may be seen by comparing the sublimation and melting points, the three hexafluorides are very similar in their physical properties. That the thermal constants do not vary uniformly as one proceeds from sulfur to tellurium, may be seen from the melting points, that of selenium hexafluoride being higher than either of those for sulfur or tellurium. Also the heats of formation show this reversal markedly, the values being in an order different from the melting points. The heats of fusion are in the same order as the melting points.

These reversals of order from the positions in the periodic table are to be found in the heats of formation of the dioxides as well, the order being the same as the heats of formation of the hexafluorides.

Experiments on the Reactivity of Selenium and Tellurium Nexafluorides

It is known from the experiments of Prideaux[2] that sulfur and selenium hexafluorides do not react with water while the tellurium compound does so slowly. Further experiments of a qualitative nature were carried out to determine if this relative inertness could be observed in other reactions.

A bulb containing selenium hexafluoride and elementary selenium was heated and observed for evidence of any reaction. No effect was noted until the glass was so hot that it began to melt, and at that point white fumes were noted. It was not possible to determine whether the reaction involved the selenium or only the glass.

The corresponding experiment in which tellurium hexafluoride and tellurium were used showed signs of reaction at much lower temperatures, dense white fumes developing when the temperature was, locally, not much above 200°. A white solid, presumably tellurium difluoride, separated in considerable amounts.

Two tubes were filied with mixtures of selenium hexafluoride and ammonia gas, the two gases having approximately the same partial pressures. One tube was placed in an electric furnace and the temperature gradually raised; at 200° traces of elementary selenium were observed; at higher temperatures the reaction proceeds somewhat more rapidly. The second tube was placed in the furnace at 330° and selenium was observed to form in increasing amounts over a period of five minutes. On breaking under water and testing the resulting solution for fluoride, an appreciable precipitate of calcium fluoride was obtained, though not as large as would be expected if no loss of detectable fluoride had occurred. The loss was due, doubtless, to the reaction of the hydrogen fluoride formed with the glass.

If Ruff's[6] value of 64,000 cal. for the heat of formation of hydrogen fluoride is used in connection with the value 11,000 cal. for ammonia and the value given in Table IV for selenium hexafluoride, then the reaction

$$2NH_3(g) + SeF_2(g) = N_2 + Se + 6HF + 116{,}000 \text{ cal.}$$

is found to take place with a large evolution of heat. The fact that the reaction does take place shows that the entropy change is not sufficiently great to make the free energy and change in heat content of opposite signs. The entropy change is doubtless such that the reaction has a very great tendency to take place over a rather large temperature range. The entropy of selenium hexafluoride would have to be about 700 cal./deg. to make $AF^\circ = 0$ and such a value is quite certain to be several times greater than the true one. Similar considerations indicate that sulfur and tellurium hexafluorides would also be reduced by ammonia or hydrogen and that sulfur hexafluoride is not to be expected as the result of a reaction between solutions of sulfuric and hydrofluoric acids. It is seen therefore that the inertness of the hexafluorides toward reducing agents cannot always be ascribed to a lack of thermodynamic tendency to react.[7]

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[6] Ruff, *Z. anorg. allgem. Chem.*, 198, 375 (1931).

[7] The results of recent electron diffraction experiments by Pauling and Brockway (private communication) show that the fluorine atoms in the hexafluorides lie at the corners of a regular tetrahedron. For sulfur hexafluoride they find the S–F distance to be 1.58 Å. From this result the entropy of sulfur hexafluoride at 25° and 1 atm. was calculated to be 62 cal./deg. It was assumed, as seems reasonable, that the vibrational entropy is small. Using this value together with the entropy of solid sulfur, 7 6 cal./deg. and fluorine 48.04 cal./deg., and the heat of formation given above, we find for

$$S(s) + 3F_2(g) = SF_6(g) \quad \Delta F^\circ_{298} = -235{,}000 \text{ cal.}$$

It is now easy to show that sulfur hexafluoride should be completely hydrolyzed by water vapor at 25° to give sulfur trioxide and hydrogen fluoride.

The Lower Volatile Fluorides of Selenium and Tellurium.—During the preparation of selenium hexafluoride a colorless liquid was observed to condense out in the train before reaching the cold traps. It was collected in a tube and the tube sealed off and set aside. On the following day the tube was found to be shattered and the fragments covered with small amounts of selenium. The liquid was evidently some lower fluoride which decomposed to form the more volatile hexafluoride and selenium or a still lower fluoride.

In the case of tellurium the purification by fractionating yielded about 1.3 cc. of a colorless liquid residue much less volatile than the hexafluoride. This residue was further fractionated and about 1 cc. of liquid obtained which was distilled under vacuum into a tube equipped with a click-gage and a series of small side tubes. After freezing with liquid air and sealing off the original container, the tube containing the liquid was surrounded by a bath of finely divided melting ice. The vapor pressure was then measured, a portion of the liquid distilled into a side tube, and the side tube sealed off. Both the side tube and main tube were cooled with liquid air before sealing to avoid the decomposition which results when the vapor is in contact with hot glass. This process was repeated until all the material had been thus distilled into seven small tubes.

The vapor pressures at 0.0° varied from 81.4 mm. for the original amount of liquid to 27.6 mm. for the last portion, thus showing that a pure product had not been obtained. The vapor densities of the second and sixth portions were determined and the results gave molecular weights of 342.0 and 341.6, respectively, showing that the composition had varied but little as a result of the fractionation. The melting point of the first fraction was found to be −13.6° and the boiling point 61.2°. An attempt was made to analyze the material for tellurium and fluorine but no precise results were obtained due to the difficulties involved. The method of preparation renders the presence of oxygen in the substance very unlikely.

Conclusions as to the nature of the substance must be based principally on the vapor density results. No tellurium fluoride molecule containing only one atom of tellurium would have a molecular weight as high as 342, since the molecular weight of TeF_6 is only 241.5. The compounds Te_2F_8 and Te_2F_6 would have as molecular weights 407.0 and 369.0, respectively, while Te_2F_2 and Te_2F_4 would have values lower than the observed one, namely, 293.0 and 331.0, respectively. From the results it is not possible to give the exact composition of the liquid material. It appears to be a mixture of two or more compounds and at least one of them contains more than one atom of tellurium in the molecule, but the formulas for these compounds cannot be given with certainty at this time.

When the liquid, enclosed in a glass tube, is placed in hot water (85° or greater), a fairly rapid decomposition takes place with the formation of a white precipitate which is presumably the difluoride. The liquid is denser than water and reacts slowly with it with the evolution of a small amount of gas, the gas in turn reacting slowly with the water in much the same manner as does the hexafluoride.

The small amount of material obtainable makes a more extensive study of the compound not feasible at this time.

Summary

The vapor pressures, melting points and sublimation points of selenium and tellurium hexafluorides have been measured and determinations of the heats of formation of the hexafluorides of sulfur, selenium and tellurium have been made. The resulting thermochemical constants of the three compounds have been calculated and presented in Table IV.

It has been found that selenium hexafluoride reacts with ammonia gas slowly at 200° and much more rapidly at 330°, to give selenium, nitrogen and hydrogen fluoride. This fact together with the thermal data has been used to show that the inertness of the hexafluorides toward reducing agents is not to be ascribed to a lack of thermodynamic tendency to react.

A lower liquid fluoride of tellurium has been discovered.

PASADENA, CALIFORNIA

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Studies on Oxidation–Reduction. XVIII. Simple Safranines

BY ROBERT D. STIEHLER, TUNG-TOU CHEN AND W. MANSFIELD CLARK

Preliminary measurements in three laboratories[1] have assigned to certain dyes of the azine group potentials which are much lower than those which characterize any indicator system discussed in the first sixteen papers of this series. For this reason azine dyes have been used in several attempts to reveal the extreme reducing ability of cells in anaerobiosis, and they have been considered as possible mediators for the potentiometric study at low potentials of "electromotively inactive" systems. However, the precision of none of the preliminary physical measurements was satisfactory and the conduct of the reductants led Cohen, Chambers and Reznikoff[2] to doubt their usefulness in the biological field. Therefore we have reexamined a few of the simpler safranines.

The potential measurements which we now report are good criteria of the primary reversibility of the oxidation–reduction process. They define

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(1) Clark and Zoller, Science, 64, 557 (1921); Vellinger, *Arch. phys. biol.*, **7**, *113* (1929); Rapkine, Struyk and Wurmser, *J. chim. phys.*, **26**, *340* (1929).

(2) Cohen, Chambers and Reznikoff, *J. Gen. Physiol.*, *11*, 585 (1928).

those more important physical characteristics which must be known. But the experiments also emphasize certain peculiarities of the components of the systems which doubtless were responsible for the uncertainties of previous measurements and which will have to be considered in the ordinary uses of these indicators. The experiments also reveal another set of cases in which there appears to be what we call a "concentration effect."

A theoretical interest in this concentration effect makes it advisable to state the nature of certain observations which may cast doubt upon the reliability of the potentials used lest the unannotated exhibit of the more concordant, calculated constants convey the impression that all possible errors have been eliminated with certainty. In the majority of instances we have observed the following. After each successive addition of reducing agent (chromous acetate), the curve relating potential to time seemed to approach an asymptotic limiting potential. After a period, varying from five to thirty minutes or more, the potentials would remain for various times within a few hundredths of a millivolt of the apparent limit. However, in those cases in which observations were prolonged it was observed that the potentials ultimately drifted to more positive values. This indicates that the minimal potentials which we have used are not those which approach an asymptotic limit as an equilibrium point but are minima resulting from the operation of two opposing effects. It is obvious that an appreciable period may be necessary for the completion of the reaction, for tautomeric rearrangements and for adjustment of the electrode; but a turn in the direction of the drift is a cause for suspicion.

One ever-present suspicion is of the presence of oxygen in the nitrogen used to deaerate and to stir the solutions. This nitrogen, originating commercially in the fractionation of liquid air, was passed through a 93 X 2.5 cm. column of copper wire at about 400". The copper wire, of 0.26 mm. diameter, cut into short lengths, was of a special, pure grade obtained through the courtesy of Mr. Charles H. Davis of The American Brass Company. The copper was repeatedly roasted and reduced in an electric furnace before use. All connections were, of course, metal or glass or, when metal to glass junctions were required, they were heavily coated inside and out with DeKhotinsky cement. Because of the finite equilibrium pressure of oxygen over heated cupric oxide and the accumulation of such oxide at the first end of the tube, it is possible that a trace of oxygen might remain. Not a trace was detected in 60 liters of the nitrogen upon employing a modification of the method of Hand,[3] which we found to give a distinct response to 1.8 X 10^{-3} mg. of oxygen. We tried the well-known method of spraying a finely divided stream of nitrogen through a filter candle into an oxygen absorbent. We used Fieser's[4] oxygen absorbent and observed no improvement of electrode conduct.

(3) Hand. *J. Chem. Soc.*, 123, [2] 2573 (1923).

(4) Fieser, THIS JOURNAL, **46**, 2639 (1924).

If the leuco dyes are more efficient absorbents than Hand's modification of Winkler's reagent, there still remains the possibility that oxidation sufficient to affect electrode potentials might have been produced by quantities of oxygen which we failed to detect. Accordingly we constructed a special cell in which all connections were sealed with mercury and in which titrations were conducted under a static layer of the purified nitrogen after a prolonged period of deaeration by the streaming nitrogen. There was no improvement of electrode conduct.

On the other hand, the behavior of the leuco dyes is suggestive. In the first place, treatment of these dyes by hydrogen and any one of several platinum or palladium catalysts produces not only a reversible reduction but a more profound change. For example, phenosafranine, exposed for eighteen hours to hydrogen in the presence of a mild platinum catalyst, suffered nearly complete destruction when buffered at P_H 1 and about 75% destruction at P_H 7. Somewhat less destruction resulted from the use of palladium deposited upon barium sulfate. In such experiments the period of exposure was long for the purpose of emphasis. A solution of the leuco compound, *immediately* after its formation by reduction, was filtered from the catalyst and retained in vacuum. A distinct color change occurred within thirty minutes; the color had deepened[5] by the following morning and when the solution was reoxidized by exposure to air about half of the original dye seemed to have been lost, according to the rather difficult colorimetric comparison between the original solution and this more complex, recovered solution. A considerable number of experiments similar to those cited above, as well as observations of the solutions titrated, have shown that in whatever manner these safranines are reduced their leuco products undergo a noticeable color change when held in buffer solutions of P_H range 3 to 7.5. This is manifested even in the reoxidized solutions by the persistence of a fluorescence different in quality from that of the original dye solutions. This fluorescence is greatly diminished by acidification of the solution.

Now, in their report upon neutral red, Clark and Perkins[6] showed that a "fluorescent material," which was isolated in crystalline form, develops in slightly acid solutions of the leuco compound, is electromotively inactive in neutral and slightly acid solutions, is rendered active by strong acid and is subject to decomposition in aqueous buffer solutions. The drifts of electrode potential were attributed to the formation of this material and to its decomposition.

In several respects the leuco safranines remind us of leuco neutral red. However, the fluorescence which develops is less distinct and a "fluorescent material" has not been isolated. We can say only that where the fluores-

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(5) No light effect comparable with that described by Clark, Cohen and Gibbs [*Public Health Reports*, **40**, 1131 (1925)] for methylene white was detected.

(6) Clark and Perkins, THIS JOURNAL, **54**, 1228 (1932).

cence has developed most distinctly, namely, in buffers of PH range, roughly, 3 to 7.5, the greater difficulties with potential measurements have occurred and the greater discrepancies in the constants calculated from these measurements have been found.

It should be emphasized that, while the foregoing remarks concerning a reversal of potential drift apply generally, the potentials in acid phosphate and acid citrate buffers were remarkably constant over considerable periods and ordinarily would be accepted as highly satisfactory. On the other hand, the attainment of constancy was very slow.

Although we can find no quantitative relation between the shift of E_0 with change of concentration and either the rate of attainment of apparent constancy of potential or the time of reversal, it may be that some kinetic effect of concentration has dominated the situation sufficiently to produce a false appearance of a shifting point of equilibrium. Since there is no evidence for this supposition, we must respect the data as they stand. There then remains the fact that when these data are put through the mathematical mill devised by Reed and Berkson[7] and briefly reviewed in the preceding paper of this series, they yield constants which are the more consistent the more stable the minimal potentials.

A fair idea of the precision attained in any one titration conducted in an unfavorable region of PH may be obtained by using as typical of the present cases the deviations from average values of E_0' found in Tables I, II and III of the previous paper on neutral red. However, the selection of favorable conditions made it possible to obtain distinctly greater precision with the simple safranines. Indeed, the reader may be surprised to find that we are reporting the fifth decimal in two instances which are typical of several. Neither the reproducibility of separate titrations nor the elimination of errors from the supplementary data which are required for the calculation of certain constants would justify this; but later we shall dwell upon an important point which can be demonstrated by means of the consistency of the values of E_0' for *any one* experiment. This is the reason for showing the extent to which the fourth decimal is "protected" in any one experiment. The apparent precision of the potentiometric readings required a comparable precision of the ratios of the buret readings. Accordingly the micro buret was calibrated with mercury to obtain precise *ratios.* In general it may be said that the magnitude of experimental errors seems to be fairly represented by discrepancies in the calculated constants.

All potential measurements were made at 30°. Previous papers of this series have described the more usual procedures, the conventions, the type of measurements used in correcting potentials for change of PH during dilution and other details. To the cases under consideration the following equation applies within limitations which will be discussed later.

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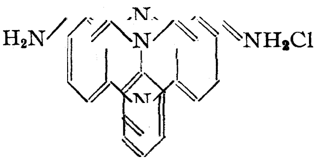
[7] Reed and Berkson, *J. Phys. Chem.*, 33, 760 (1929).

$$E_h = E_0 + 0.03006 \log \frac{[S_0]}{[S_R]} + 0.03006 \log [(H^+)^3 + K_{r_1}(H^+)^2 + K_{r_1}K_{r_2}(H^+)] \qquad (1)$$

Here E_h is the potential in volts, referred to the hydrogen standard; $[S_0]$ is the molar concentration of total oxidant; $[S_R]$ is the molar concentration of total reductant; (H^+) is the hydrion activity; $K_{r_1} = (H^+)(H_2^+Red)/(H_3^+Red^+)$; $K_{r_2} - (H^+)(HRed)/(H_2Red^+)$. At constant hydrion activity the last term of (1) becomes constant. Then at unit ratio of total oxidant to total reductant and specification of the PH number, we write $E_h = E_0'$. In the tables y indicates the milliliters of reducing agent actually used and d the correction for residual oxidizing impurities estimated by the method of Reed and Berkson.[7]

Experimental

Phenosafranine (Rowe **840**).[8] I.—A commercial preparation was recrystallized twice from methanol. The product was dried to constant weight over phosphorus pentoxide. ***Anal.*** (Kjeldahl). Calcd. for $C_{18}H_{15}N_4Cl$: N, 17.37. Found: N, 17.4, 17.3.



I

In Table I are summarized the results of individual titrations and the calculations therefrom. Here there is evident the effect of the particularly rapid change which takes place in leuco phenosafranine between PH 3 and 7. Within that range the general tendency of the observed values of E_0' to be positive to our best placement of the calculated values, made after a consideration of the E_0':PH curve as a whole, probably gives a fair representation of the errors. The concentration effect will be discussed later.

TABLE I

PHENOSAFRANINE. RELATION OF E_0' TO PH

Determined by individual titrations with chromous acetate at 30°. Values used in calculations: $K_{r1} = 1.12 \times 10^{-5}$ ($pK_{r1} = 4.95$), $K_{r2} = 1.67 \times 10^{-6}$ ($pK_{r2} = 5.78$), $E_0 = 0.2800$ at $-\log C = 4.52$; 0.2790 at $-\log C = 3.52$. C = concentration of total dye at 50% reduction.

Buffer	PH	−log C	E_0' Found	E_0' calcd.	Found − calcd.
HCl	1.079	4.52	+0.1823	+0.1827	−0.0004
Citrate	2.004	4.52	.0991	.0993	− .0002
Citrate	2.005	3.52	.0982	.0982	.0000
Phosphate	2.124	4.53	.0885	.0885	.0000
Citrate	2.735	3.52	.0323	.0324	− .0001
Citrate	2.735	3.52	.0323	.0324	− .0001
Citrate	3.194	4.52	− .0031	− .0078	+ .0047
Citrate	3.194	4.52	− .0041	− .0078	+ .0037
Citrate	3.195	3.52	− .0058	− .0089	+ .0031
Citrate	3.195	3.52	− .0057	− .0089	+ .0032

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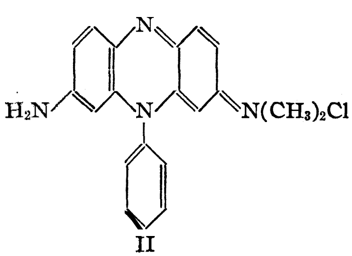
(8) Rowe, "Colour Index," **Society of Dyers and Colourists**, 1924.

TABLE I *(Concluded)*

Buffer	p_H	$-\log C$	E'_0 found	E'_0 calcd.	Found − calcd
Citrate	3.453	4.52	−0,0274	−0.0310	+0.0036
Citrate	3.453	4.52	− .0274	− .0310	+ .0036
Citrate	3.445	3.52	− .0270	− .0313	+ .0043
Acetate	4.076	4.52	− .0862	− .0859	− .0003
Acetate	4.972	4.52	− .1581	− .1580	− 0001
Citrate	5.448	4.52	− .1849	− .1888	+ .0039
Citrate	5.448	4.52	− .1840	− .1888	+ .0048
Citrate	5.449	3.52	− .1839	− .1898	+ .0060
Citrate	5.723	4.52	− .2008	− .2035	+ .0027
Phosphate	6.082	4.52	− .2180	− .2197	+ .0017
Phosphate	7.105	4.52	− .2558	− .2555	− .0003
Borate	8.622	4.52	− .3017	− .3017	.0000
Phosphate	11.097	4.52	− .3760	− .3760	.0000

Dimethyl Phenosafranine (Fuchsia, Rowe 842). 11.—For the sample used we are indebted to Dr. Max Phillips. He prepared it according to the method of Bindschedler.[9] The dye was salted out of solution with sodium chloride and crystallized from 95% ethanol. A qualitative test showed that the dye had not been completely freed from salt by this crystallization, a fact which may account for the low nitrogen. *Anal.* (Kjeldahl). Calcd. for $C_{20}H_{19}N_4Cl$: N, 15.98. Found: N, 15.0, 15.1. The potentiometric measurements indicated a homogeneous dye.



II

As in the case of phenosafranine, so in the case of the dimethyl derivative the titrations were satisfactory when conducted with acid phosphate and acid citrate buffers and moderately good when conducted with alkaline solutions. In the intermediate range the results with dimethyl safranine were much better than those with phenosafranine. Table II represents one of the titrations conducted under favorable circumstances.

Upon assembling the values of E_0, calculated from a considerable number of those titrations which were conducted under the more favorable conditions, the discrepancies were judged to be much larger than the recognized experimental errors would allow. There was then applied the empirical equation (2)

$$\tilde{E}_0 = E_0 + 0.0044 \log C \qquad (2)$$

where C is the molar concentration of total dye at 50% reduction. A fairly good resolution of the discrepancies is evident in Table III. An exception is the first recorded case in which we can trace no source of error.

In Table IV are assembled the results of three series of measurements made as follows. To each buffer solution was added an aliquot of the

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(9) Bindschedler, *Ber.*, 16, 869 (1883).

TABLE II

TITRATION OF DIMETHYL PHENOSAFRANINE WITH CHROMOUS ACETATE AT 30°

Approximate composition of buffer: 0.1 M **citric acid,** 0.05 **M** NaOH per **liter. Solution titrated:** 75 ml. **buffer** + 5 ml. buffered, 0.001 M **dye.** Chromous **acetate diluted 1:1 with double strength buffer. Log concn. dye at** 50% **reduction** = —4.22. **P**H = 2.960.

y ml. corr. (Buret A)	$y - d$	$\log (y - d)$	$\log (A - y + d)$	0.030055 $\log \frac{y - d}{A - y + d}$	E_h	E_0'	Deviation from av.
0.496	0.316	−0.5003	0.7258	−0.03685	0.05665	(0.01980)	(+0.00013)
0 794	0.614	− .2118	.7008	− .02743	.04709	.01966	− .00001
1.091	0.911	− .0405	.6743	− .02148	.04111	.01963	− .00004
1.387	1.207	+ .0817	.6462	− .01697	.03654	.01957	− .00010
1.685	1.505	.1775	.6160	− .01318	.03280	.01962	− .00005
1.983	1.803	.2560	.5834	− .00984	.02953	.01969	+ .00002
2.287	2.107	.3237	.5475	− .00673	.02640	.01967	.00000
2.589	2.409	.3818	.5087	− .00381	.02353	.01972	+ .00005
2.892	2.712	.4333	.4658	− .00098	.02065	.01965	− .00002
3.194	3.014	.4791	.4185	+ .00182	.01787	.01969	+ .00002
3.496	3.316	.5206	.3653	.00467	.01504	.01971	+ .00004
3.797	3.617	.5583	.3049	.00762	.01208	.01970	+ .00003
4.099	3.919	.5932	.2345	.01078	.00890	.01968	+ .00001
4.397	4.217	.6250	.1517	.01423	.00538	.01961	− .00006
4.702	4.522	.6553	.0465	.01830	+ .00140	.01970	+ .00003
5.001	4.821	.6831	− .0894	.02322	− .00348	.01972	+ .00005
5.298	5.118	.7091	− .2865	.02992	− .00995	(.01997)	(+ .00030)
5.596	5.416	.7337	− .6596	.04188	− .02026	(.02162)	(+ .00195)
A =	5.635						
					Average =	.01967	
					E_0 =	.28656	

TABLE III

DIMETHYL PHENOSAFRANINE. EFFECT OF CONCENTRATION

Results of individual titrations with chromous acetate. C = **molar concn. of dye system at** 50% **reduction.** $\tilde{E}_0 = E_0 + 0\ 0044 \log C$.

Buffer	Pa	E_0'	E_0	$-\log C$	$\tilde{E}_0$	Deviation from 0.2680
Phosphate	2.123	0.0956	0.2867	4.60	0.2666	−0.0014
Phosphate	2.693	.0405	.2833	3.38	.2684	+ .0004
Citrate	2.960	.0199	.2866	4.22	.2680	.0000
Citrate	3.094	.0064	.2852	3.97	.2677	− .0003
Citrate	3.101	.0039	.2832	3.38	.2683	+ .0003
Citrate	3.495	− .0273	.2873	4.33	.2682	+ .0002
Citrate	3.493	− .0271	.2874	4.32	.2684	+ .0004
Citrate	3.552	− .0355	.2842	3.67	.2681	+ .0001
Citrate	3.549	− .0367	.2827	3.39	.2678	− .0002
Citrate	3.557	− .0375	.2827	3.38	.2678	− .0002
Acetate	4.621	− .1262	.2849	3.79	.2682	+ .0002
Acetate	4.627	− .1283	.2833	3.38	.2684	+ .0004
Citrate	6.209	− .2302	.2827	3.38	.2678	− .0002

dye solution. After deaeration, one aliquot of a chromous acetate solution was added to the mixture and the minimal potential was recorded. This method permits no correction for the variable quantities of oxidizing impurities in the buffer solutions and consequently some irregularities are to be expected. However, it is only in a few cases that these are larger than the irregularities experienced with the more detailed method and since the E_0': PH curve is well defined for acid regions by the comparable data of Table III, the more refined method was not applied extensively to neutral solutions.

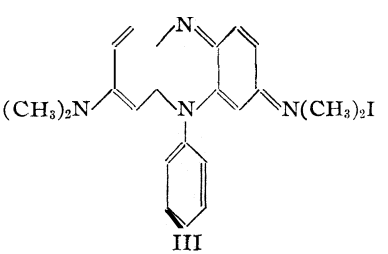
TABLE IV

DIMETHYL PHENOSAPRANINE. RELATION OF E_0' TO PH AT 30°

Determined by addition of one aliquot of chromous acetate solution to each mixture of dye and buffer. Subsequent orientation at 50% reduction by starred values obtained from Table III. Log C at 50% reduction, —3.66. Values used in calculations: $K_1 = 1.26 \times 10^{-5}$ ($pK_1 = 4.90$). $K_2 = 4.68 \times 10^{-7}$ ($pK_2 = 6.33$), $E_0 = 0.2841$.

Series	Buffer	PH	E_0' obs	E_0' calcd.	E_0' obs. − E_0' calcd
I	HCl	1.114	0.1837	0.1837	0.0000
	Phosphate	2.696	.0417	.0411	+ .0006
	Citrate	3.096	.0065	.0052	+ .0013
	Citrate	3.552	− .0356*	− .0356	.0000
	Acetate	4.607	− .1263	− .1258	− 0005
	Phosphate	6.847	− 2504	− .2557	+ .0053
	Borate	8 597	− .3119	− .3117	− 0002
II	Citrate	3 552	− .0356*	− .0356	.0000
	Acetate	4 996	− 1561	− .1555	− .0006
	Citrate	5.365	− .1785	− .1808	+ 0023
	Citrate	6 794	− 2066	− .2069	+ ,0003
	Citrate	6.217	− .2298	− .2291	− .0007
	Phosphate	7 222	− .2689	− .2589	.0000
	Borate	7 960	− .2940	− .2925	− .0015
	NaOH + KC1	12 304	− .4225	− .4233	+ .0008
III	Citrate	3.552	− .0356*	− .0356	.0000
	Acetate	4.236	− .0951	− .0953	+ .0002
	Citrate	5.794	− .2064	− ,2069	+ .0005
	Borate	8 185	− .3004	− ,2992	− ,0012
	Borate	8.597	− .3127	− .3117	− .0010
	Borate	9.704	− 3449	− ,3451	+ ,0002
	Phosphate	11.296	− .3909	− .3929	+ .0020
	NaOH + KCl	12 309	− 4220	− 4234	+ 0008

Tetramethyl Phenosafranine (Iodide). 111.—After having made several titrations of a sample of the chloride and having found the slopes of the titration curves to be suggestive of a mixture of dyes, we appealed to Dr. Leslie Hellerman for a satisfactory preparation. He followed in the main the method of Bindschedler[10] with care for the purity of the reagents used in making Bindschedler's green, regard for the ease with which this intermediate is hydrolyzed (see Phillips, Clark and Cohen)[11] and the cautious oxidation of the mixture of Bindschedler's green and aniline to the safranine. The crude chloride contained considerable impurity and was



III

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(10) Bindschedler *Ber.*, 16, 867 (1883); *cf.* Nietzke, *ibid.*, 16, 472 (1883).

(11) Phillips, Clark and Cohen, Public *Health* Reports, Supplement 61 (1927).

very resistant to crystallization. The iodide was prepared as follows. To a dilute aqueous solution of the crude material an excess of potassium iodide was added. The small crystals which formed were separated by filtration, thoroughly washed with water and recrystallized twice from ethanol. The substance was dried to constant weight at 110° over phosphorus pentoxide. *Anal.* (Kjeldahl). Calcd. for $C_{22}H_{23}N_4I$: N, 11.92. Found: N, 11.8, 11.6. This material gave titration curves as of a homogeneous dye. Table V summarizes data sufficient to define the E_0':*P*H curve.

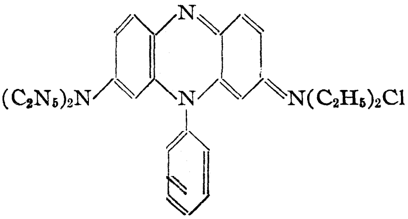
TABLE V

TETRAMETHYL PHENOSAFRANINE (IODIDE) RELATION OF E_0' TO *PH*

Determined by individual titrations with chromous acetate at 30". Values used in calculations: $K_{r1} = 4.79 \text{ X } 10^{-6}$ ($pK_{r1} = 5.32$). $K_{r2} = 3.55 \text{ X } 10^{-7}$ ($pK_{r2} = 6.45$). $E_0 = 0.2896$. Log *C* (at 50% reduction) = —4.60.

Buffer	PH	E_0' found	E_0' calcd	Pound − calcd
Citrate	2.966	+0.0221	+0.0222	−0.0001
Acetate	4 082	− .0780	− .0777	− .0003
Acetate	4 984	− 1547	− .1547	.0000
Citrate	5.855	− 2157	− .2166	+ .0009
Phosphate	6.478	− 2513	− .2498	− .0015
Phosphate	7.311	− 2820	− .2822	+ .0002
Borate	8 248	− 3118	− .3118	0000

Tetraethyl Phenosafranine (Amethyst **Violet,** Rowe 847). **IV.—For** the sample used we are indebted to Professor H. Bucherer of Munich. The material contained zinc and presumably was the zinc chloride double salt. We attempted to recrystallize this material but found difficulty in recovering an amount of clean crystals sufficient for our titrations.



(Zinc double salt)
IV

The potentials observed with this compound in acid solution were very stable. Table VI contains a good set of data indicative of a homogeneous material. In neutral and alkaline buffers the free base of the reductant separates from solutions as dilute as 1 X 10^{-5} molar with consequent distortion of the titration curve. By working rapidly and considering the first section of each titration curve we obtained rough estimates of E_0' values, but the details need not be stated since the graphic representation in Fig. 1 is adequate for the precision obtained in neutral and alkaline solutions. The estimated dissociation exponents, 6.4 and 7.7, are only crude approximations.

Safranine T (Safranine O) Rowe 841.—The original commercial sample bore the label "Safranine O, Schultz 679"[12] and the certification

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(12) *This* number undoubtedly refers to the 1014 edition of "Farbstofftabellen" by Schultz. In the edition of 1931 the number is 967.

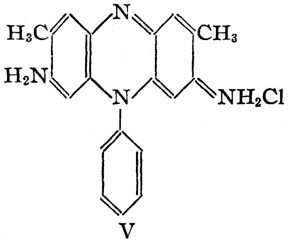
TABLE VI

AMETHYST VIOLET. TITRATION WITH CHROMOUS ACETATE AT 30°

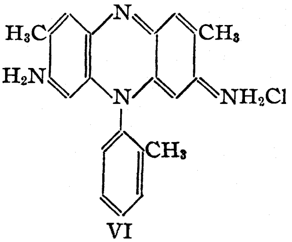
Approximate composition of buffer: 100 ml. 1 M KH_2PO_4 + 50 ml. 1 *M* HCl, diluted to 1 liter. Solution titrated: 75 ml. buffer + 10 ml. 0.00076 M dye (uncorr.). Reference PH (that of 75 ml. buffer + 10 ml. water) 2.118. Log concn. of dye at 50% reduction = –4.06 (uncorr.). Correction of E_h for change of PH due to dilution, 0.17 mv. per ml.

Y (*Buret* B)	*y* − *d*	Reduction, %	0.030066 log $[S_R]/[S_o]$	E_h corr.	E_0'	Deviation from average
0.2	0.117	4.68	−0.03905	+0.20369	(0.16464)	+0.00020
.4	.317	12.68	− .02518	.18953	.16435	− .00009
.6	.517	20.68	− .01754	.18190	.16436	− .00008
.8	.717	28.68	− .01188	.17636	.16448	+ .00004
1.0	.917	36.68	− .00713	.17164	.16451	+ .00007
1.2	1.117	44.68	− .00279	.16726	.16447	+ .00003
1.4	1.317	52.68	+ .00139	.16307	.16446	+ .00002
1.6	1.517	60.68	.00566	.15882	.16448	+ .00004
1.8	1.717	68.68	.01025	.15418	.16443	− .00001
2.0	1.917	76.68	.01553	.14888	.16441	− .00003
2.2	2.117	84.68	.02232	.14220	.16452	+ .00008
2.4	2.317	92.68	.03313	.13280	(.16593)	+ .00149
	2.500	100.00				
				Average	.16444	
				E_0 =	.3554	

No. PS-2 of the Commission on Standardization of Biological Stains. It probably consisted of a mixture of dyes V and VI as stated by Rowe.



V



VI

TABLE VII

SAFRANINE T. TITRATION WITH CHROMOUS ACETATE AT 30°

Approximate composition of buffer: 100 ml. 1 *M* citric acid + 35 ml. 1 M NaOH diluted to 1 liter. Solution titrated: 75 ml. buffer + 5 ml. 0.0005 M dye. Reference *P*H (that of 75 ml. buffer + 5 ml. water) 2.738. Log *C* at 50% reduction = –4.53. Correction of E_h for change of PH due to dilution, 0.17 mv. per ml.

y	*y* − *d*	Reduction, %	0.03006 log $[S_R]/[S_o]$	E_h corr.	E_0'	Deviation
0.5	0.27	3.67	−0.0426	0.0364'	(−0.0062)	+0.0016
1.5	1.27	17.26	− .0205	.0127	− .0078	.0000
2.5	2.27	30.84	− .0105	.0028	− .0077	+ .0001
3.5	3.27	44.43	− .0029	− .0048	− .0077	+ .0001
4.5	4.27	58.02	.0042	− .0120	− .0078	.0000
5.5	5.27	71.60	.0121	− .0198	− .0077	+ .0001
6.5	6.27	85.19	.0228	− .0307	− .0079	− .0001
7.5	7.27	98.78	.0574	− .0653	− .0079	− .0001
A	= 7.36	100		Average	− .0078	

By crystallization, first from warm 95% ethanol and again from absolute ethanol, the material gave large, clean needles of uniform appearance. These retained "moisture" tenaciously. When brought to constant weight by intensive drying they yielded 15.7 and 15.6% nitrogen The theoretical value corresponding to formula V is 15.98% N and that corresponding to formula VI is 15.41% N.

The results of the potentiometric measurements were surprisingly like those of a homogeneous dye, as Table VII clearly indicates. If our crystallization has not isolated such a dye it must be that the characteristic potentials of the component dyes are nearly the same. Table VIII summarizes the results.

TABLE VIII

SAFRANINE T, RELATION OF E_0' TO PH

Determined by individual titrations with chromous acetate at 30°. Values used in calculations: $K_{r1} = 1.95 \times 10^{-5}$ ($pK_{r1} = 4.71$). $K_{r2} = 1.82 \times 10^{-6}$ ($pK_{r2} = 5.74$), $E_0 = 0.2381$. Log C at 50% reduction, —4.53.

Buffer	PH	E_0' obs.	E_0' calcd.	Deviation
HCl	1.093	+0.1386	+0.1395	−0.0009
Citrate	2.738	− ,0078	− .0086	+ .0008
Acetate	4.620	− .1707	− .1703	− .0004
Acetate	4.985	− .1972	− .1961	− .0011
Acetate	5.218	− .2112	− .2109	− .0003
Citrate	5.425	− .2224	− .2229	+ .0005
Phosphate	6.090	− .2540	− .2541	+ .0001
Phosphate	6.496	− .2688	− .2692	+ .0004
Phosphate	7.106	− .2884	− .2890	+ .0006
Borate	8.629	− .3356	− .3354	− .0002
Borate	9.679	− .3671	− .3670	− .0001
Phosphate	10.94	− .4049	− .4049	.0000
NaOH + KCl	12.32	− .4464	− .4464	.0000

Supplementary Data

To extend the study of the concentration effect, parallel measurements at two concentrations were made with each of the dyes listed in Table IX. In this series of experiments the strength of the acid phosphate buffer was made double that used in previous experiments in order to provide a further check by lowering the error due to changes in acidic and basic components during titration. Of course the effect of dilution upon the PH value of the buffer remained and in each instance it was determined by hydrogen electrode measurements of dilutions made in this instance, not by water, but by an oxidized solution of the chromous acetate reducing agent. Since the buffer strength was such as to give an ionic strength approximately twice that of comparable previous experiments, the constants of Table IX are not strictly comparable with those of previous experiments (see footnote 15, page 906).

Titrations of reduced solutions of the safranines with oxidizing agents were also made. For the reasons already stated the results were not precise but they indicated that no serious peculiarities had been introduced by dependence upon the titrations with chromous acetate.

In Table X are summarized some spectrophotometric measurements which will be discussed later.

TABLE IX

EFFECT OF CONCENTRATION OF DYE SYSTEM UPON E_0

Results of titrations with chromous acetate in 0.2 M KH_2PO_4 + 0.1 M HCl

Oxidant of system	Log concentration −3.79 E_0	−4.60 E_0	$\Delta E/\Delta \log C$
Phenosafranine	0.2817	0.2825	−0.0010
Tetramethyl phenosafranine	.2905	.2923	− .0022
Tetraethyl phenosafranine	.3557	.3606	− .0060
Safranine T	.2342	.2382	− .0050

See also Table III.

TABLE X

ALTERATION OF ABSORPTION MAXIMA

C = molar concentration of dye

Compound	−log C	Absorption max. in mμ	Observer	Nature of solution
Phenosafranine	2.82	515	Holmes	Aqueous
	4.21	520	Holmes	Aqueous
	3.0	515	S. C. and C.	Phosphate buffer P_H 2.1
	5.0	520	S. C. and C.	Phosphate buffer P_H 2.1
Dimethyl phenosafranine	3.0	530	S. C. and C.	Phosphate buffer P_H 2.1
	5.0	550	S. C. and C.	Phosphate buffer P_H 2.1
Tetramethyl phenosafranine	3.0	542	S. C. and C.	Phosphate buffer P_H 2.1
	5.0	578	S. C. and C.	Phosphate buffer P_H 2.1
Tetraethyl phenosafranine	3.0 uncorr.	552 (588)	S. C. and C.	Phosphate buffer P_H 2.1
($ZnCl_2$ double salt)	5.0 uncorr.	588	S. C. and C.	Phosphate buffer P_H 2.1
Safranine T	3.0	492	S. C. and C.	Phosphate buffer P_H 2.1
	5.0	518	S. C. and C.	Phosphate buffer P_H 2.1
Methylene blue	3.04	600	Holmes	Aqueous
	5.40	663	Holmes	Aqueous
Nile blue	2.74	580	Holmes	Aqueous
	4.66	635	Holmes	Aqueous
	2.74	578	Cohen and Preisler	Aqueous
	5.05	630	Cohen and Preisler	Aqueous

Discussion

The potentiometric and other measurements demonstrate that each of the several systems is, primarily, reversible. However, the reductants are subject to progressive alterations which should be seriously considered as limiting the reliability of these dyes as oxidation–reduction indicators.

With reservations to be discussed later, the data satisfy equation (1). From this fact and the attendant numerical values of the constants may be drawn some interesting conclusions. Each of the graphic representations of the relation of E_0' to P_H, as shown in Fig. 1, exhibits a section where $\Delta E_h/\Delta P_H = -0.09016$ and a section where $\Delta E_h/\Delta P_H = -0.03006$. The intersection of projections of these sections (or the corresponding algebraic relations) determines the values of $^1/_2(pK_{r_1} + pK_{r_2})$ and hence

$K_{r_1}K_{r_2}$. Since these distinct sections of each curve are fairly well placed, the value of $K_{r_1}K_{r_2}$ is determined rather well. On the other hand, the greater difficulties of measurement and the consequent uncertainties of calculation are encountered in that region of PH where the inflections of the curves occur and there the very highest accuracy is required for the evalu-

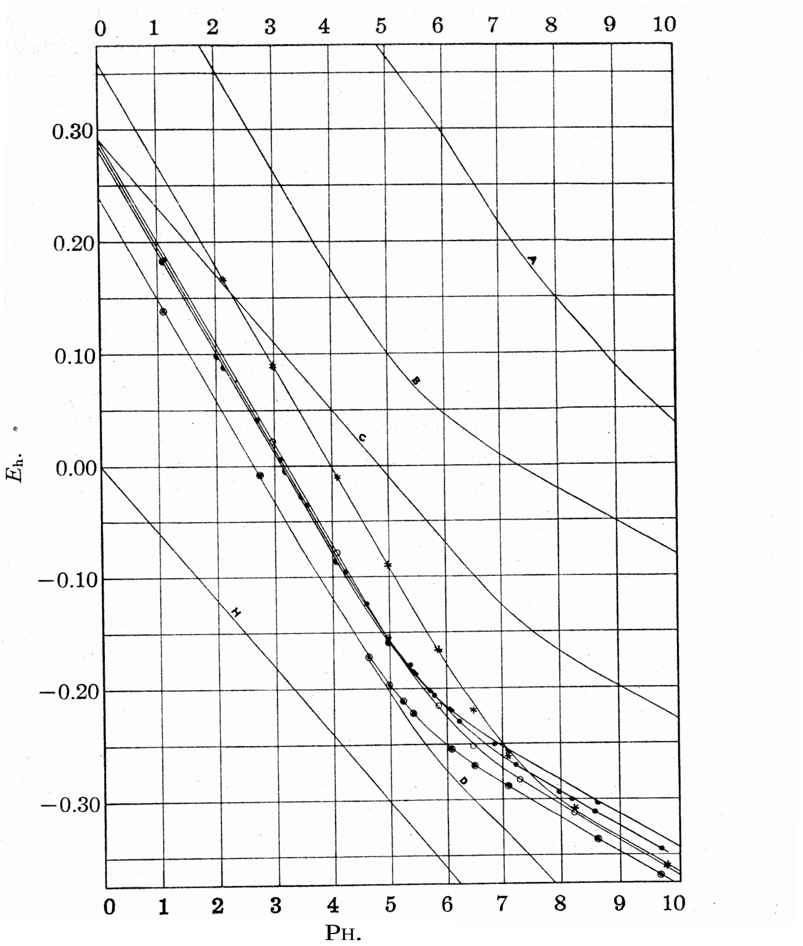


Fig. 1.—Relation of E_h to PH at 50% reduction of dye (E_0':PH curve).

Experimental

-▾- Phenosafranine at log C = −4.52
-◉- Dimethyl phenosafranine at log C = −3.66
-⊖- Tetramethyl phenosafranine at log C = −4.60
* Tetraethyl phenosafranine at log C = −4.53 (uncorr.)
-⊙- Safranine T at log C = −4.53

Comparisons

A. 2,6-Dibromophenolindophenol
B. Methylene blue
C. Indigo disulfonate
D. Neutral red
(H. Hydrogen at 1 atm.)

ation of the individual dissociation constants. Hence these individual values are not well known. The refinements used in the tables are for purposes of definite calculation. However, there can be no doubt that there have been established relations similar to those of the methylene blue system.[5] The structural allocation of dissociation constants in the case of the components of the methylene blue system was confirmed by comparisons with the data for Lauth's violet, for Bindschedler's green and for toluylene blue,[11] an assembly of data in which dissociation constants not measurable in one instance were apparent in another instance. Since the safranines are similar to Lauth's violet and methylene blue as regards basic groups, there is good reason to assume the following. The predominant form of each oxidant of the safranines is the paraquinone structure, indicated by the formulas I–VI, resulting in a "polar" group so strongly basic that the dissociation exponent does not come within the reach of our experiments. The other amino, or substituted amino group, of each oxidant is so weakly basic that its dissociation exponent also does not come within the reach of our experiments. Therefore, we have to deal with one predominant form which may be represented by the symbol Ox^+. Upon reduction the molecule attains a more symmetrical structure, and the dissociation exponents fall within the range 4.7 to 7.7. Indeed in any one compound they are so close as to obscure the intermediate "0.06-slope" of the E_0':*P*H curve (see Fig. 1). The influence of strengthening basicity is evident in Fig. 1 where the E_0':*P*H curves for the tetramethyl and the tetraethyl phenosafranines, which fall above the curve for phenosafranine at low ***Pa***, cross this curve and then run below it at high PH.

In Fig. 1 the E_0':*P*H curves of 2,6-dibromophenolindophenol, methylene blue and indigo carmine and also the curve of the hydrogen electrode (at 1 atmosphere H_2) are included to show the relative positions of the safranine oxidation–reduction systems. There is also included the curve for neutral red from PH 4.5 to 7.9. This curve shows the structural influence upon the course in alkaline solution. It runs parallel and very close to the curve for safranine T in acid solution, the values of E_0 being: neutral red, 0.240; safranine T, 0.238.

With that caution which has already been noted regarding a possible systematic error, we may now discuss the "concentration effect." In the case of phenosafranine the situation is not entirely clear. The measurements in buffer solutions of PH range 3 to 7.5 were particularly subject to drifts and the resulting errors are evident alike in Table I and Fig. 1. However, if we confine attention to the more acid solutions, there appears in Table I about a millivolt increase of E_0 per tenfold dilution of the dye system. This is confirmed by the data of Table IX. With the other systems the "concentration effects" are more distinct (see Tables III and IX).

There seems to apply, within the range of concentrations used, the empirical equation (2a)

$$\tilde{E}_0 = E_0 + A \log C \tag{2a}$$

where A is 0.001 for phenosafranine, 0.0044 for dimethyl phenosafranine, 0.0022 for tetramethyl phenosafranine, 0.006 for tetraethyl phenosafranine and 0.005 for safranine T. Similar relations have been reported by Clark, Cohen and Gibbs,[5] whose somewhat discordant data for methylene blue may be expressed by equation (2a) and the coefficient 0.0154 between log $C = -3.0$ and -4.0, and by Cohen and Preisler[13] whose consistent data for Nile blue at PH 4.88 and the range of concentration between 1×10^{-4} molar and 1×10^{-5} molar give the coefficient 0.0166. In each of the instances there have been encountered difficulties with the potential measurements which might have introduced a systematic error; but the difficulties have been of a different nature in the three distinct series of cases and if systematic errors have been wrongly interpreted as a "concentration effect," they have yielded a remarkably consistent relation.

In commenting upon the case of methylene blue Clark, Cohen and Gibbs noted that their data included the range of concentration within which Holmes[14] had found remarkable changes in the wave lengths of maximal absorption by the oxidant. In conformity with Holmes' statement that all the oxazine, thiazine and azine dyes which he examined exhibit this effect, Cohen and Preisler found an instance in Nile blue and we have found instances with the dyes under discussion. The data are summarized in Table X. Since the change of an absorption maximum is not continuous with dilution but rather is a replacement of one maximum by another, it would be improper to attempt a direct correlation between the magnitude of a "shift" and a coefficient of equation (2a). It can only be said that the spectroscopic evidence of a change in the species of the oxidant is associated with a change in the characteristic potential of the system.

This and other evidence which suggested that the change of species might be a change in state of aggregation led Cohen and Preisler to the tentative postulation of a *reversible* change in the state of aggregation of Nile blue as a means of accounting for the change of potential with dilution. If this could be proved, accurately controlled potentiometric measurements could be used in the very important calculation of the free energy of aggregation. However, if the change of potential be attributed to a change in the state of aggregation of the oxidant alone, the effect should be revealed not only in parallel titrations with different concentrations but also in any one titration. A tenfold dilution of the oxidant occurs in passing from the state of 9% reduction to the state of 90% reduction of the system. This should alter the calculated value of E_0' by one millivolt in the case of pheno-

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(13) Cohen and Preisler, Public *Health* Reports, Supplement 92 (1931).

(14) Holmes, Ind. Eng. *Chem.*, 16, 35 (1924).

safranine and by several millivolts in other cases. While the data for certain titrations of phenosafranine doubtless could be recalculated in such a way as to furnish the predicted small distortion for this system, neither the data of Tables II and VI nor the data of several other of the more precise titrations would submit to such treatment. It is only to indicate this that we have reported, with proper qualifications, the fifth decimal in the cases cited and have completed the elaborate calculations in other cases.

There remain to be considered certain aspects of the theoretically more complete equations. A discussion of this may be abbreviated if we confine attention to the acid solutions where the predominant species are Ox^+ and $H_3^+Red^+$ (see page 904). These are involved in the process.

$$\mathrm{Ox}^+ + 2e + 3\mathrm{H}^+ \rightleftharpoons \mathrm{H}_3^+\mathrm{Red}^+$$

Let ( ) indicate activity, [ ] molar concentration and γ activity coefficient. The electrode equation is then **(3)**

$$E_h = \frac{RT}{2F} \ln \frac{(\mathrm{Ox}^+)(\mathrm{H}^+)^3}{K(\mathrm{H}_3^+\mathrm{Red}^+)} \tag{3}$$

or at constant hydrion activity

$$E_h = \frac{RT}{2F} \ln \frac{B}{K} + \frac{RT}{2F} \ln \frac{[\mathrm{Ox}^+]}{[\mathrm{H}_3^+\mathrm{Red}^+]} + \frac{RT}{2F} \ln \frac{\gamma_0}{\gamma_r} \tag{4}$$

where

$$\frac{RT}{2F} \ln \frac{B}{K} = E_0'$$

The last term of equation (4) could hardly be altered appreciably by that contribution to the ionic strength of the heavily buffered solution which is made by the relatively very small quantities of the components of the dye system. Consideration of the complete equation, involving all species, leads to a similar conclusion. Therefore some factor other than ionic strength[15] must alter the ratio of activity coefficients.

Thus it appears that neither the ionic strength effect nor a change in the state of aggregation of the oxidant alone can account for the "concentration effect."

It is possible that the more careful titrations, which were designed to reveal the association of the oxidant, were confined to a range of concentration unsuited to the purpose. This possibility is now under examination.

We wish to express our appreciation of the contributions made by the persons mentioned in the text and especially of the aid given by Dr. Leslie Hellerman and Miss Marie Perkins.

Summary

With a precision adequate for the ordinary uses of the dyes as oxidation-reduction indicators there have been determined the characteristic con-

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[15] The ionic strength effect has not been subjected to direct experiment in this series of cases There are *a priori* reasons for believing the effect to be much smaller than that demanded of the relation $(RT/nF) \ln (\gamma_0/\gamma_r) = 0.045 \sqrt{\mu}$ which would obtain under the *limiting law* of Debye and Hückel. A comparison of the data of Table IX, obtained with an acid phosphate buffer of $\mu = 0.21$, with the data of cases where the ionic strength was about 0.1, indicates this and also that there is no consistent relation between the coefficients of equation (2a) and the effect of ionic strength.

stants of the systems which are named below by the names of the respective oxidants. A reversal of potential drift during measurements has been ascribed to a secondary, irreversible alteration of reductant similar to but not so extensive as that previously reported in the case of leuco neutral red. The least interference by this effect was encountered in acid phosphate and acid citrate buffers of PH < 3. While an undetected systematic error may still persist in such cases, the data indicate that the "normal potential," E_0, is a function of the concentration, C, of the dye system as expressed by the relation

$$E_0 = \tilde{E}_0 - A \log C$$

This cannot be due to the relatively small contributions of components of the dye systems to the ionic strengths of the solutions. Apparently precise measurements in individual titrations have shown that a reversible change in the state of aggregation of the oxidant alone, as tentatively proposed by Cohen and Preisler for the case of Nile blue, cannot be applied in the present instances. Some change of species of each oxidant is, however, indicated by the spectrophotometric comparisons of relatively dilute and concentrated solutions of these dyes.

At a fixed concentration of dye system and approximately constant ionic strength the following relation holds in each instance

$$E_h = E_0 + \frac{RT}{2F} \ln \frac{[S_O]}{[S_R]} + \frac{RT}{2F} \ln [(H^+)^3 + K_{r1}(H^+)^2 + K_{r1}K_{r2}(H^+)]$$

where $[S_0]$ = molar concentration of total oxidant, $[S_R]$ = molar concentration of total reductant, (H^+) = hydrion activity, and $K_{r_1} = (H_2^+Red)(H^+)/(H_3^+Red^+)$, $K_{r_2} = (HRed)(H^+)/(H_2^+Red)$.

For convenience the data of the text have been reduced to comparable values for 0.0001 M and constants are rounded off in the table, all values at 30°.

At $C = 1 \times 10^{-4}$ *M*

Dye	E_0	E_0' at PH 7.0	$\frac{\Delta E}{A \log C}$	K_{r1}	pK_{r1}	K_{r2}	pK_{r2}
Phenosafranine (Rowe 840)	0.280	−0.252	−0.001	1.1×10^{-5}	4.95	1.7×10^{-6}	5.8
Dimethyl *phenosafranine (Rowe* 842)	.286	− .260	− .0044	1.3×10^{-5}	4.9	4.7×10^{-7}	6.3
Tetramethyl phenosafranine	.288	− .273	− .0022	4.8×10^{-6}	5.3	3.6×10^{-7}	6.5
Tetraethyl phenosafranine (Rowe 847)	.355	− .254	− .006	4×10^{-7}	6.4	2×10^{-8}	7.7
Safranine T (Rowe 841)	.235	− .289	− .005	2×10^{-5}	4.7	2×10^{-6}	5.7

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The Dielectric Constant of Solutions of Amino Acids and Peptides

BY JEFFRIES WYMAN, JR., AND T. L. MCMEEKIN

I. Introduction

Ever since the introduction of the zwitter ion hypothesis in the papers of Küster[1] and Bredig[2] more than thirty years ago it must have been apparent that one of the outstanding properties of these ions would be their abnormally large electric moments, determined by the distance separating the oppositely charged acid and basic groups.[3] Although it is impossible to determine electric moments quantitatively in polar solvents, where if at all the existence of zwitter ions may be expected, it is nevertheless possible to make qualitative estimates of them from the values of the dielectric constant, and in the course of the last ten years a number of investigations of the dielectric constant of aqueous solutions of amino acids and related compounds have been carried out to test the validity of the hypothesis on this basis.[4] In spite of quantitative differences these results as a whole afford good evidence in favor of the zwitter ion concept.

In view of the interest of the question, the discrepancies among previous results, and above all the need for more extensive data, the present investigation was undertaken. This comprises a study of the dielectric constant of a number of amino acids dissolved in water, of one also in solution in alcohol water mixtures, and of aqueous solutions of the first six peptides of glycine. The results are of interest however not only in connection with the zwitter ion hypothesis but also on account of evidence they afford as to the configuration of the molecules.

II. Experimental Procedure

The method employed for the determination of the dielectric constant was one recently described by the writer,[5] based on the principle of resonance and yielding absolute values. The frequency was between about 1.5 X 10^8 and 6 X 10^7 cycles (in terms of wave length, between 2 and 5 meters) and was varied in a number of cases over a twofold range in view of

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(1) Küster, Z. *anorg. Chem.*, *13*, 135 (1897).

(2) Bredig, Z. *Elektrochem.*, **6**, 33 (1899).

(3) Assuming the distance separating the amino and carboxyl groups in glycine to be 3 Å. in accordance with x-ray data, we obtain a value of about 14 X 10^{-18} e. s. u. for the electric moment. The largest moment reported for an un-ionized molecule is 7.1 X 10^{-18} in the case of 1,8-dinitronaphthalene, and this is several times the moment of most compounds.

(4) See Fürth, Ann. *Physik*, **70**, 63 (1923); Blüh, Z. *physik. Chem.*, **106**, 341 (1923); Walden and Werner, *ibid.*, 129, 389 (1927); Hedestrand, *ibid.*, 136, 36 (1928); Devoto, *Gazz. chim. ital.*, **60**, 520 (1930); 61, 897 (1932). These results were obtained with several different methods at frequencies ranging from about 5 X 10^8 to 10^6 cycles per second.

(5) Wyman, *Phys. Rev.*, **35**, 623 (1930).

a possible dependence of dielectric constant on it. However, even in the case of the largest molecule studied (the hexapeptide of glycine), no evidence of dispersion was apparent, which is in accordance with an analysis of the data of previous investigators. The accuracy of the individual determinations of dielectric constant was about 0.1%. The measurements were, for the most part, made at 25°. In some cases, however, determinations were made at a variety of temperatures and the figures for 25° obtained by interpolation.

III. Preparation sf Materials

The α-amino acids used in the investigation were recrystallized from commercial material from alcohol–water mixtures until the analytical results indicated a high degree of purity.

β-Alanine.—β-Alanine was prepared by treating β-bromopropionic acid with a large excess of ammonia. After removing ammonia, β-alanine was purified by recrystallization from alcohol, m. p. 198°; nitrogen, 15.80%.

β-Aminobutyric Acid.—β-Aminobutyric acid was prepared by the method of E. Fischer and Groh,[6] m. p. 188–190°; nitrogen, 13.50%.

γ-Aminovaleric Acid.—γ-Aminovaleric acid was obtained from the Chemistry Department of the University of Illinois. It was further purified by recrystallization from alcohol, nitrogen 12.0%.

a-Aminocaproic Acid.—We are indebted to Dr. J. T. Edsall of the Harvard Medical School for the preparation of ε-aminocaproic acid. This substance was prepared by the method of Wallach[7] and melted sharply at 199–200°.

Glycine Peptides.—Peptides of glycine were prepared by the well known methods of E. Fischer.' Each of the peptides was reprecipitated from alcohol–water mixtures until salt free. Total and a-amino nitrogen determinations were made on each.

Glycine-&peptide.—Total nitrogen found 21.00%.calcd. 21.21%; a-amino nitrogen found,[8] 10.96%, calcd. 10.60%.

Glycine-tripeptide.—Total nitrogen found, 22.58%, calcd. 22.23%; a-amino nitrogen found, 7.64%, calcd. 7.41%.

Glycinetetrapeptide.—Total nitrogen found 22.84%, calcd. 22.77%; a-amino nitrogen found 5.39%, calcd. 5.69%.

Glycine-pentapeptide.—Total nitrogen found 22.95%, calcd. 23.10%; a-amino nitrogen found 4.68%, calcd. 4.62%.

Glycine-hexapeptide.—Total nitrogen found 23.50%, calcd. 23.38%; a-amino nitrogen found 3.68%, calcd. 3.89%.

IV. Results on Aqueous Solutions

It was found in all cases, in agreement with previous results of Hedestrand[4] and of Devoto,[4] that the dielectric constant of the solutions was, within the limits of experimental error, a linear function of the concentration, expressed in moles per liter at 25°, up to the highest concentration

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(6) Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine," 1899–1906, Julius Springer, Berlin, 1906; Vol. II, 1907–1919, Julius Springer, Berlin, 1923.

(7) Wallach, *Ann.*, 313, 171 (1900).

(8) The "found" value was obtained by multiplying the experimental value by 0.8. Abderhalden and Van Slyke [*Z. physiol. Chem.*, 74, 606 (1911)] found that glycine peptides gave high a-amino nitrogen values. but if the values obtained were multiplied by 0.8, the result was very close to the theoretical value.

TABLE I

Substance	Range of concn. studied	Density at concn. c	Specific conductivity (ohms^{-1}) at concn. c	δ at 25° (author's value)	Other values of δ at temp. t
Glycine (NH_2CH_2COOH)	0.0–2.5	1.0569, $c = 2.0$		22.58	23.0, $t = 18^a$ 26.4, $t = 25^b$
α-Alanine ($CH_3NH_2CHCOOH$)	.0–0.8904		103 × 10^{-6}, $c = 0.8904$	23.16	23.57, $t = 18^a$ 6.4, $t = 19.6$
α-Aminobutyric acid ($CH_3CH_2NH_2CHCOOH$)	.0– .7355			23.16	
α-Aminovaleric acid ($CH_3CH_2CH_2NH_2CHCOOH$)	.0– .47	1.0051, $c = 0.329$		22.58	
β-Alanine ($NH_2CH_2CH_2COOH$)	.0–1.182			34.56	42.25, $t = 18^a$
β-Aminobutyric acid ($CH_3NH_2CHCH_2COOH$)	.0–0.7849	1.0182, $c = 0.7849$	308 ×10^{-6}, $c = 0.7849$	32.36	
γ-Aminovaleric acid ($CH_3NH_2CHCH_2CH_2COOH$)	.0– .1826	1.0023, $c = .1826$	1725 ×10^{-6}, $c = .4566$	54.8	
ϵ-Aminocaproic acid ($NH_2CH_2CH_2CH_2CH_2CH_2COOH$)	.0– .1335		12000 ×10^{-6}, $c = .890$	77.5	
Glycine-dipeptide	.0– .1050	1.0030, $c = .1050$	54[illegible] ×10^{-6}, $c = .1050$	70.6	70 $t = 25^b$
Glycine-tripeptide	.0– .06523	1.0017, $c = .0622$	19000 ×10^{-6}, $c = .06523$	113.3	
Glycine-tetrapeptide	.0– .05962	1.00275, $c = .05962$	42800 ×10^{-6}, $c = .05962$	159.2	
Glycine-pentapeptide	.0– .02639	1.00012, $c = .02639$	53100 ×10^{-6}, $c = .02639$	214.5	
Glycine-hexapeptide	.0– .01315		46800 ×10^{-6}, $c = .01315$	234.2	

[a] Hedestrand (4).

[b] Devoto (4).

[c] Walden and Werner (4).

studied (2.5 molar in the case of glycine). On this account it is unnecessary to list the individual values of the dielectric constant obtained and the data may be exactly expressed in terms of the increase of dielectric constant per mole of dissolved material, a quantity which, for brevity, we denote by 6, and which is accordingly defined by the relation

$$\delta = \frac{\epsilon - \epsilon_0}{c}$$

where ϵ is the dielectric constant of the solution, ϵ_0 that of water, and c the concentration of the ampholyte in moles per liter. The data so expressed for all the substances studied are given in Table I. In all cases where it was measured, the specific conductivity of the solutions and data on the density are also included; in addition, the results of previous observers, in so far as they exist, are added for comparison in the last column of the Table.[9]

The results on glycine were extended over a wider range of temperature than in the other cases and it was found that the variation of δ with temperature was remarkably slight, though definite. The values are given in Table II. The increase of 6 with diminishing temperature may be regarded as further evidence, in addition to the fact that the results are independent of wave length, against the possibility of dispersion at these frequencies.

TABLE II

THE EFFECT OR TEMPERATURE ON THE DIELECTRIC CONSTANT OF SOLUTIONS OF GLYCINE IN WATER. RANGE OF CONCENTRATION STUDIED 0.0–2.0 MOLES PER LITER

Temperature, °C.	0	5	10	15	20	25
δ	23.80	23.43	23.14	22.94	22.78	22.58

V. Confirmation of the Zwitter Ion Hypothesis

In order to interpret the foregoing results we may assume with confidence that the greater the dielectric constant of a solution, of given molar concentration, in a given solvent, the greater the electric moment of the dissolved molecules, exactly as in the case of ideal solutions in non-polar solvents. More specifically, we will assume that the values of 6, defined above, correspond in magnitude with the values of the electric moments of the ampholytes, and base our considerations on these in what follows.

In accordance with this conception the foregoing results greatly strengthen the argument in favor of the predominance of zwitter ions in the cases studied. (a) In all the new instances, as well as the old, the values of 6 are positive and much larger than in the case of any of the non-ampholytes thus far studied. For example, for most of these δ is negative, and even in the case of urea and related substances, which are exceptional in raising the dielectric constant of water, δ is not greater than about 4. It is interesting to observe in this connection that the anhydride of glycyl-

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[9] Since Fürth's results failed to show a linear relation between dielectric constant and concentration, it is impossible to give a value of 6 for comparison.

glycine, studied by Devoto, behaves like other non-electrolytes, in marked contrast to the peptide itself. It is also worth pointing out that the only amino acids so far investigated which have failed to produce an increase in the dielectric constant, namely the o-, m- and *p*-aminobenzoic acids studied by Hedestrand, are just those estimated by Bjerrum[10] and Ebert[11] on the basis of dissociation constants not to exist predominantly in the zwitter ion form. (b) The value of δ is very nearly the same for all four α-amino acids as, likewise, in the case of two β acids. A similar constancy was observed by Devoto among a large group of a-amino acids and Hedestrand found a close agreement between glycine and a-alanine. This suggests that the electric moments of these molecules in solution arise from their properties as zwitter ions and do not depend appreciably on specific chemical differences. (c) The same thing is also indicated by the progressive increase of δ with the distance separating the amino and carboxyl groups in the molecule. This is shown very impressively by the results on the γ- and ϵ-amino acids and by the series comprising the peptides of glycine. This latter series lends support to a previous interpretation given by the author[12] to observations on the dielectric constant of solutions of the protein zein in alcohol–water mixtures, where, owing to the great size of the molecule and the high viscosity of the solutions, the results are obscured by phenomena of anomalous dispersion.

VI. The Configuration of the Molecules

As already pointed out the present results afford evidence as to the configuration of the molecules. It would not be unnatural to suppose that the longer molecules, both the amino acids and the peptides, have a tendency to bend back upon themselves and possibly to form rings. This might be expected both in accordance with the tetrahedral model of the carbon atom, and on the general grounds that such a bending, bringing the positively and negatively charged ends of the molecule closer together, would diminish the electric moment and cause a reduction of the associated potential energy. It has, moreover, been suggested on more specific grounds by several observers.[13] In particular, Astbury and Woods[1*] have concluded, on the basis of x-ray studies, that the protein molecules in unstretched wool fibers have a looped structure in which there is an alternation of five and seven numbered rings; on the other hand, in stretched wool fibers and in silk fibers under all conditions the molecules are stated to consist of an essentially linear arrangement of amino acids.

The present results appear to be definitely inconsistent with the idea of

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(10) Bjerrum, Z. *physik.* Chem , 104, 147 (1923).

(11) Ebert, *ibid* , 121, 385 (1926).

(12) Wyman, J. *Biol.* Chem., 90, 443 (1931).

(13) Notable in this connection are observations of Svedberg that the majority of protein molecules subjected to a strong centrifugal force settle in accordance with Stokes' formula for spheres. See T. Svedberg, various papers since 1926 in THIS JOURNAL.

(14) Astbury and Woods, Nature, 126, 913 (1930).

bending or ring formation in the case of the molecules studied in solution. The steady increase of electric moment with the length of chain separating the oppositely charged groups, which has been so clearly shown and which is taken as a strong argument in favor of the zwitter ion hypothesis, could only be expected and can indeed only be accounted for on the assumption of straight, rod-like molecules. If there were any considerable bending of the molecules, the carboxyl and amino groups would actually be expected to approach nearer together as the length of the chain is increased. For example, on the basis of the structure attributed by Astbury and Woods to the molecules of unstretched wool fibers the moment of glycylglycine should actually be less than that of glycine itself (in fact, about half).

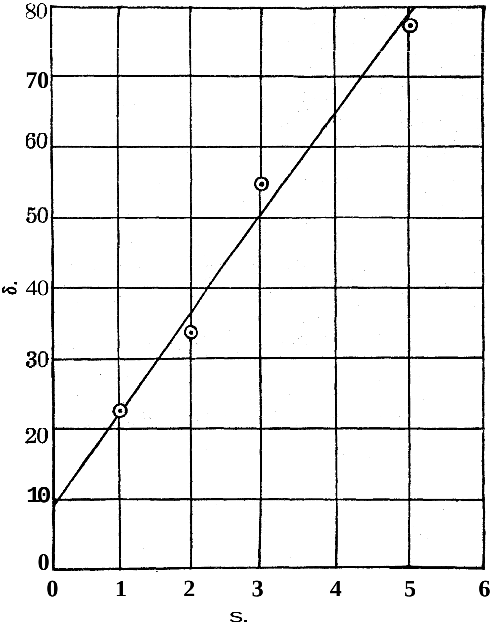

Fig. 1.

In regard to the question of the rod-like form of the molecules it is of interest to consider exactly how far 6 is in fact proportional to the distance between the oppositely charged groups in the zwitter ion, assuming the ion to be straight. This is illustrated by the two accompanying figures. In Fig. 1 values of 6 for the amino acids studied are plotted against this distance, expressed in terms of the number of carbon atoms (n). In Fig. 2 values of δ for the peptide series, including glycine itself, are plotted against the number of glycine units (N) in the molecule.

VII. Results on Glycine in Alcohol–Water Mixtures

On the basis of a consideration of dissociation constants in alcohol, Ebert[11] has estimated that the formation of zwitter ions must be greatly reduced in this solvent. In regard to this point, it is of interest, therefore, to consider the data on the dielectric constant of solutions of glycine in ethyl alcohol–water mixtures. The data were obtained by the authors using the same method employed for aqueous solutions. Owing to the decrease of solubility of glycine with increasing concentration of alcohol, the measurements were not extended beyond 60% alcohol. The results are given in Table III.

TABLE III

Per cent. alcohol	6
0.0, $\epsilon_0 = 78.54$	22.58
20.0, $\epsilon_0 = 69.96$	22.47
40.0, $\epsilon_0 = 59.69$	21.67
60.0, $\epsilon_0 = 47.88$	20.56

These figures show a surprisingly small change of δ with change of the percentage alcohol in the solvent, which would indicate that, even in the case of 60% alcohol, the zwitter ion predominates. It must not be overlooked, however, that since estimates of the ratio of zwitter ions to un-ionized molecules is of the order 1000 to 1, or 10,000 to 1, a many-fold change in the ratio would still leave the zwitter ion predominant.

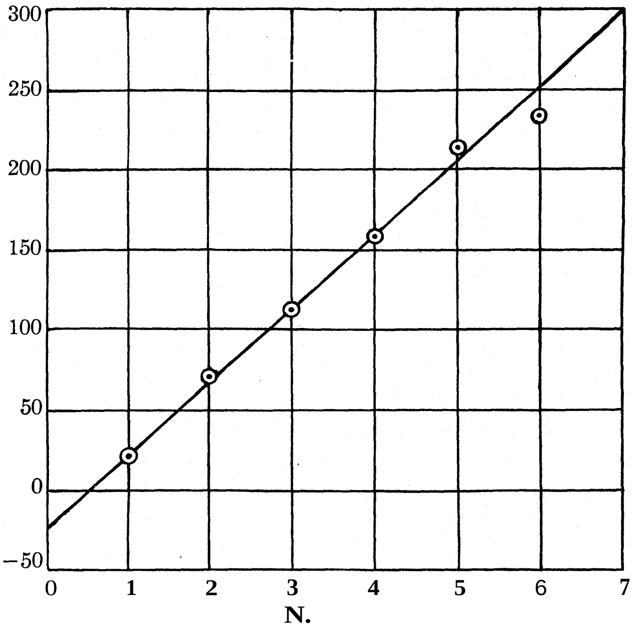

Fig. 2.

VIII. Summary

Measurements of the dielectric constant of a variety of amino acids of the α, β, γ and ϵ types and of five peptides of glycine, in aqueous solution, afford additional evidence in favor of the zwitter ion hypothesis. The results indicate that all the molecules studied are rod-like structures without tendency to bending or formation of rings. Measurements of solutions of glycine in alcohol–water mixtures indicate that in these cases too the zwitter ions are predominant.

CAMBRIDGE AND BOSTON, MASSACHUSETTS

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[FROM THE DEPARTMENT OF ZOÖLOGY, HARVARD UNIVERSITY, AND THE DEPARTMENT OF PHYSICAL CHEMISTRY IN THE LABORATORIES OF PHYSIOLOGY, HARVARD MEDICAL SCHOOL]

The Dipole Moments of Esters of Amino Acids and Peptides

BY JEFFRIES WYMAN, JR., AND T. L. MCMEEKIN

I. Introduction

In the preceding paper in THIS JOURNAL it was pointed out that qualitative estimates of the electric moments of amino acids and peptides, in solution in water and alcohol–water mixtures afford strong evidence that these substances exist in the form of zwitter ions: (a) the moments are all abnormally large; (b) they are the same for all amino acids of a given type; (c) they show a linear increase with the length of chain separating the acid and basic groups in the molecule.

The argument just outlined, however, convincing as it is, leaves out of consideration the possibility of these effects being explained in terms of electric moments inherent in the un-ionized molecules. For example, in regard to the first point, it is not certain that the undissociated amino acids and peptides are not themselves sufficiently polar to account directly for the high values of the electric moment observed. In regard to the last point, it is not wholly clear that the differences of electric moment between the various types of amino acids may not be due to the different orientation of certain groups, or that the greater moments of the larger peptides may not be due to the greater size of the molecules. It was in order to investigate these possibilities and to place the argument on a more secure basis that the present investigation was undertaken. This comprises an exact determination of the electric moments, in the un-ionized condition, of as many of the compounds previously studied in water and alcohol–water mixtures as was possible. The results however have a certain independent interest in themselves.

IIa. Choice of Materials

The ideal procedure would have been to dissolve each of the substances in some non-polar solvent, such as benzene, in which the formation of zwitter ions would undoubtedly be suppressed and in which alone it is possible to make quantitative measurements of moments in accordance with the theory developed by Debye.[1] Unfortunately, however, none of the ampholytes in question are appreciably soluble in any of the non-polar solvents, no doubt for the very reason that ionization cannot take place. In view of this difficulty, it was decided to study the esters, many of which are readily soluble in benzene. In particular, the ethyl esters were selected in preference to the methyl ones, as being more stable.

Ample justification for applying the values obtained for the moments

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(1) Debye, "Polar Molecules," Chemical Catalog Company, Inc., New York. 1929.

of the esters to the acids themselves is to be found in the well-known generalization that the substitution of a hydrogen atom by a methyl or ethyl group has very little effect on the moment of the molecule involved.[2]

Unfortunately, even by using this procedure, it was not possible to study all the materials in question. Although the esters of the amino acids themselves are readily soluble in benzene, it was found that the esters of the peptides were very insoluble, to an extent increasing with the number of glycine units in the molecule. For this reason, it was only possible to study one of the peptides, glycylglycine, and even this was only sufficiently soluble for measurement at 50°. Another difficulty was encountered in the case of the ester of y-aminovaleric acid, which was found to pass over rapidly into the anhydride.[3] The anhydride thus unintentionally obtained was found to be soluble in benzene and was included among the compounds measured. In view of the instability of the ester of γ-aminovaleric acid no attempt was made to study the esters of any of the δ or ϵ acids.

A list of the substances investigated, with references to the method of preparation, is given in the following section. In addition to observations on the boiling points, or melting points, and, in the case of the anhydride, analytical data on the nitrogen content, determined by the Kjeldahl method, this list also gives values of the density ρ and index of refraction n, both at 25°. The density was measured with a pycnometer. In the case of the esters of glycine, a-alanine and β-alanine, the index of refraction was determined for red light with an Abbé refractometer made by Bausch and Lomb; in all other cases, for sodium light with a Pulfrich–Zeiss instrument. In the case of the ester of glycylglycine, which melts at 86°, these data on the density and index of refraction are lacking.

IIb. Preparation of Materials

All a-amino acids used as starting materials in the preparation of the esters were obtained from the Eastman Kodak Company. They were recrystallized from alcohol–water mixtures before using.

Glycine Ethyl Ester.—Glycine ethyl ester was made by the well-known Fischer[4] method of preparing esters of amino acids; boiling point 43–44° at 12 mm. pressure; $\rho = 1.0169$; $n = 1.4213$.

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[2] This is illustrated by the following data taken from the appendices to Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Inc., New York, 1931.

Substance	Moment (e. S. u. 10^{-18})
Acetic acid	1.73
Methyl acetate	1.75
Ethyl acetate	1.81
Propionic acid	1.74
Ethyl propionate	1.79

[3] This is not surprising since the usual method of preparation of the anhydride is through the ester as an intermediate stage.

[4] Pischer, *Ber.*, 34, 433 (1901); 34, 2868 (1901).

α-Alanine Ethyl Ester.—α-Alanine ethyl ester was prepared by the method of Fischer; boiling point 48–52' at 12 mm. pressure; ρ = 0.9722; n = 1.4155.

α-Aminobutyric Acid Ethyl Ester.—This ester was also prepared by the method of Fischer;[4] boiling point 60–62° at 12 mm. pressure; p = 0.9533; n = 1.42070.

α-Aminovaleric Acid Ester.—This compound was prepared by the method of Slimmer;[5] boiling point 73–75' at 12 mm. pressure; p = 0.9377; n = 1.4241.

α-Valine Ethyl Ester.—The method of Slimmer[5] was used to prepare this compound; boiling point 66–70' at 12 mm. pressure; p = 0.9390; n = 1.4267.

a-Aminocaproic Acid Ethyl Ester.—The method of Fischer[4] was used to prepare this compound; boiling point 91–92° at 12 mm. pressure; p = 0.9246; n = 1.42829.

l-Leucine Ethyl Ester.—Fischer's[4] method was used to prepare this compound; boiling point 82–84' at 12 mm. pressure; p = 0.9215; n = 1.42655.

β-Alanine Ethyl Ester.—The method of S. Hoogewerff and van Dorp[6] was used to prepare this substance; boiling point 56–58' at 12 mm. pressure; p = 0.9892; n = 1.4250.

β-Aminobutyric Acid Ethyl Ester.—The method of Fischer and Groh[7] was followed in the preparation of this compound; boiling point 60–62° at 12 mm. pressure; p = 0.9409; n = 1.4221.

Glutamic Acid Diethyl Ester.—This compound was prepared by the method of Fischer;[4] boiling point 140–142° at 12 mm. pressure; p = 1.0620; n = 1.44045.

Glycylglycine Ethyl Ester.—Fischer's[4] method was used to prepare this substance; melting point 86° (uncorrected).

Anhydride of γ-Aminovaleric Acid.—The method of Tafel[8] was used to prepare this substance; boiling point 132–135° at 12 mm. pressure; nitrogen, found 14.20%; calcd. 14.14%; p = 1.0288; n = 1.4695.

IIc. Determination of Electric Moments

The values of the electric moments were calculated from data at a single temperature in dilute solutions in benzene in the usual way. This procedure involves a knowledge of the total and optical polarizations, P_1 and P_{10}, of the solute at a variety of concentrations. From the value of $P_1 - P_{10}$ extrapolated to zero concentration the electric moment is calculated from the expression

$$\mu = 0.0127\,(P_1 - P_{10})T \times 10^{-18} \text{ e. s. u.}$$

where T is the absolute temperature.[1]

The determination of P_1 requires the direct measurement of the density and dielectric constant of the solution, together with a knowledge of its composition. For this purpose the values of the density were measured with a chainomatic immersion densitometer, which greatly facilitated the measurements, particularly at high and low temperatures. The accuracy of the determinations was between 0.02 and 0.03%, and, although this is much less than that attainable with a pycnometer, the errors were well below those involved in measurements of the dielectric constant and were not significant.

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(5) Slimmer, *Ber.*, 36, 400 (1902).

(6) Hoogewerff and van Dorp, *Rec. trav. cham.*, 10, 4 (1891).

(7) Fischer and Groh, Ann. *Chem. Pharm* , 383, 363 (1911)

(8) Tafel, Bcr., 19, 2414 (1886).

The method employed for the determination of the dielectric constant was the same as in the study of solutions of the free acids and peptides described in the previous paper.[9] Owing, however, to the much lower values of the dielectric constant of the benzene solutions, it was necessary to use a far larger resonator in order to keep the resonance points within the frequency range of the oscillator (lower wave length limit about 2.2 meters). This introduced a problem in regard to the amount of solution required, for it is essential to the method that the resonator be immersed in a volume of material sufficient to include sensibly its entire electric field. In order to reduce this volume as far as possible a special type of resonator was constructed having a minimum stray field. This is shown, in vertical section, in the accompanying figure, together with the glass container for the solution and a glass jacket to allow the circulation of water to control the temperature. This circuit consisted of three concentric brass cylinders, the inner and outer ones being connected and forming one plate of a condenser. The opposite plate, formed by the middle cylinder and separated from the two others by a clearance of 0.8 mm., was supported rigidly by the single brass loop forming the inductance. Small holes were appropriately drilled to allow the entrance of liquid and the escape of air when the resonator was immersed, and the whole structure was heavily gold-plated to provide a clean surface. This circuit had a resonant wave length of 4.193 meters in air and of about **6.3** meters in the benzene solutions (depending on the exact value of the dielectric constant). With this arrangement it was possible to make absolute measurements of the dielectric constant on only 60 cc. of solution.

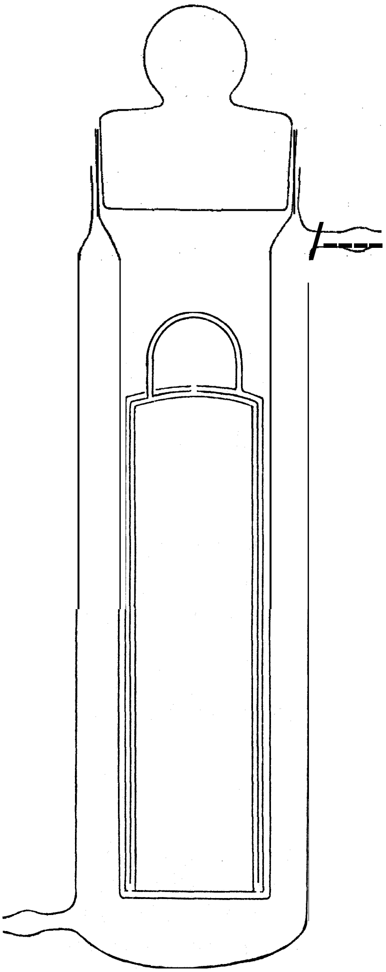

Fig. 1.

Before accepting the results obtained with this resonator, it was necessary to investigate the extent of errors due to residual stray lines of force extend-

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[9] Wyman, *Phys. Rev.*, **35**, 823 (1930).

ing out into the glass and surrounding water. Owing to the shielding effect of the outer cylinder, these were bound to be small, but at the high frequencies involved there was the possibility of capacity effects along the surface of the outer cylinder and across the loop forming the inductance, which might be expected to spread out into the surrounding media to an appreciable extent. To ascertain the magnitude of these, determinations were made of the resonant wave length of the circuit under the following conditions: (a) suspended freely in air; (b) in the bottle filled with air and standing on the table; (c) in the bottle filled with air and jacketed with water. The values obtained in the first two cases were indistinguishable. The value obtained in the last case was 0.17% higher. When benzene was substituted for air the resonant wave length determined according to conditions (c) was 0.13% too high. Since the dielectric constant is given by the square of the ratio of the resonant wave length in the solution divided by the resonant wave length in air, it is evident that these small errors nearly cancel one another and involve a net error of less than 0.08% in the dielectric constant. Since this is scarcely more than the random errors involved in the measurements, no attempt has been made to correct for these effects in the following results.

The values of the optical polarization P_{10} were for the most part calculated from the data on the density and index of refraction of the pure compounds given above. In the case of glycylglycine, however, owing to the high melting point, no attempt was made to measure directly the density and refractive index of the pure material. Instead, the optical polarization was determined indirectly from the density and index of refraction of the benzene solutions, together with the optical polarization of benzene itself, in exactly the same way that the total polarization P_1 is calculated from corresponding data on the density and dielectric constant.

III. Results

In the case of glycine and β-alanine the measurements were extended over a range of temperature from 5 to 75° in order to test the constancy of $(P_1 - P_{10})T$, which is to be expected on theoretical grounds (see Debye (1)). The results are given in Table I.

TABLE I

Temp., °C.	$(P_1 - P_{10})T$	Temp., °C.	$(P_1 - P_{10})T$
Glycine Ethyl Ester		Alanine Ethyl Ester	
5	28,200	5	29.000
20	28,000	20	29,500
30	26,800	30	29,000
50	27,600	45	28,300
70	28,100	60	28,000
		75	27,500

The values of $(P_1-P_{10})T$ listed in the table were derived by extrapolation to infinite dilution from results obtained on dilute solutions. Despite a considerable fluctuation, attributable mainly to difficulties of temperature control at the upper and lower limits, it is clear that the values of $(P_1 - P_{10})T$ show no systematic variation with temperature. In this respect these esters are like the majority of other substances which have been studied and behave in accordance with the standard theory.

The results of the entire investigation are summarized in Table II. This contains the following data for each of the esters: the optical polarization P_{10}; values of $(P_1 - P_{10})T$ tabulated against mole fraction of the ester; the limiting value of $(P_1 - P_{10})T$, extrapolated to infinite dilution, given in parentheses; the corresponding dipole moment μ; the temperature at which the measurements were made.

TABLE II

Ester	Temp., °C.	P_{10}	Mole fraction	$(P_1 - P_{10})T$	Mole fraction	$(P_1 - P_{10})T$	Dipole moment, μ
Glycine ethyl ester	5–75	25.73	0.0175	27,600			2.11 X 10^{-18}
			,00882	27,700			
			(.00000)	(27,700)			
a-Alanine ethyl ester	25	30 20	.0530	29,000	0.0175	28,700	2.09×10^{-18}
			.0422	29,000	.00875	27,100	
			.0294	29,100	(.00000)	(27,000)	
a-Aminobutyric acid ethyl ester	25	34.90	.0778	24.000	.0113	29,100	2.13×10^{-18}
			.0530	26,600	.00679	28,600	
			.0350	28,300	(.00000)	(28,000)	
			.0208	29,600			
a-Aminovaleric acid ethyl ester	25	39.50	.03577	27,600	.01106	28,100	2.13×10^{-18}
			.02665	28,100	.005505	28,300	
			.01853	28,300	(.000000)	(28,000)	
Ethyl ester of α-amino-valine	25	39.66	.02968	28,400	.01646	27,800	2.11×10^{-18}
			.02065	28,200	(.00000)	(27,700)	
a-Aminocnproic acid ethyl ester	25	44.31	.03223	27,000	.00807	27,700	2.13×10^{-18}
			.02563	27,100	.00645	29,300	
			.02041	27.500	(.00000)	(28,000)	
			.01627	28,000			
β-Alanine ethyl ester	5–75	30.27	.0264	29,100	.00296	27,500	2.14×10^{-18}
			.00757	28,700	(.00000)	(28,500)	
β-Aminobutyric acid ethyl ester	25	35.42	.0397	25,900	.0099	27,400	2.11×10^{-18}
			.027	26,300	(.0000)	(27,700)	
			.01644	27,200			
Leucine ethyl ester	25	44 37	.0377	25,100	.0116	24,800	2.03×10^{-18}
			,0280	25,600	.00693	25,520	
			.0195	25,800	(.00000)	(25,500)	
Diethyl ester of glutamic acid in C_6H_6	25	50.54	.03924	38,900	.008193	41,500	2.56×10^{-18}
			.03113	39,600	.006130	40,400	
			.02314	39,800	(.000000)	(40,600)	
			,01374	39,000			
Ethyl ester of glycylglycine	50	42.6	.01763	65,600	.006689	66,000	3.20×10^{-18}
			.01405	66,800	(.000000)	(63,500)	
			.01120	67,100			
Anhydride of y-amino-valeric acid	25	26.87	.05542	28,600	.01024	38,300	2.62×10^{-18}
			.04189	30,000	.00464		
			.02930	31,810	(.00000)	(42,500)	
			.01464	38.100			

IV. Discussion

So far as the authors are aware, there have been no previous determinations of the moments given in this table. It is of interest however to compare them with Estermann's[10] values of 1.4 X 10^{-18} and 2.7 X 10^{-18} for the methyl esters of α- and 6-aminovaleric acids, respectively. The discrepancy between the former of these and the authors' value of 2.13 for the ethyl compound is far too great to attribute to the difference between the ethyl and methyl groups, and no other explanation suggests itself. In regard to the latter result, it appears possible that in reality the ester had passed over spontaneously into the anhydride before the measurement was made, as in the case of the y-acid studied by the authors. In fact their value of 2.62 $\times$ 10^{-18} for the moment of the anhydride of γ-valeric acid is close to Estermann's figure of 2.7 X 10^{-18} for what he supposed to be free δ-amino form.

None of the moments listed in Table II are large, and it appears reasonably certain that the high values of the dielectric constant of the aqueous solutions of the free acids must depend on the effect of the zwitter ions. Further support in favor of this view may be drawn from the moments of the methyl esters of *m* and *p* aminobenzoic acids, reported by Estermann[10] as 2.4 and **3.3** $\times$ 10^{-18}, respectively. Although both of these are greater than the moments of glycine and most other amino acids listed above, the free acids form aqueous solutions of dielectric constant less than that of water. This is, of course, readily intelligible in terms of the zwitter ion theory when it is recalled that calculations based on dissociation constants indicate that the aminobenzoic acids dissolved in water do not exist mainly in the ionized form.[11]

Another strong argument in favor of the zwitter ion hypothesis, which provides an answer to one of the objections raised at the outset of this paper, is the close agreement between the moments of the esters of the α and β acids, in marked contrast to the behavior of the free acids in aqueous solution. The slightly lower moment of the leucine ester was at first attributed to the branched structure of the molecule but this appears unlikely in view of the results on valine which also has a branched chain. It is in any case relatively unimportant. The large moment of the ester of glutamic acid is undoubtedly due to the presence of two carboxyl groups.

Another objection referred to in the introduction, namely, that the progressive increase in the electric moments of the peptides of glycine in aqueous solution with the size of the molecule might be due to the greater inherent moments of the larger molecules, associated with the possession of

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(10) Estermann, Z. *physik. Chem.*, **B1**, 134 (1928).

(11) Bjerrum, ibid., 104, 147 (1923). Similar considerations might be advanced in regard to glycylglycine and glycylglycine anhydride. Although data on the moment of *the* anhydride are lacking, it may be assumed by analogy with the anhydride of γ-aminovaleric acid that this is greater than in the case of the peptide itself. Nevertheless, solutions of glycylglycine have dielectric constants greater than water, those of the anhydride, less [see Devoto, *Gazz. chim. ital.*, *61*, 897 (1932)].

a greater number of polar groups, rather than to the formation of zwitter ions, is not conclusively answered by the present results. Nevertheless, in a general way they are against it. The moment obtained for the ester of glycylglycine is only half again as great as that of the ester of glycine itself. On the other hand, in contrast to this, the data on the dielectric constant indicated that the electric moments of the peptides in aqueous solution were directly proportional to the number of glycine units in the molecule, as if due to the formation of zwitter ions. It is unfortunate that their great insolubility in non-polar solvents makes it impossible to measure the moments of the esters of the higher peptides.

V. Summary

Highly approximate values of the electric moments of amino acids and peptides have been obtained from measurements on solutions of the esters in benzene. An analysis of these results furnishes additional support for the zwitter ion hypothesis.

CAMBRIDGE AND BOSTON, MASSACHUSETTS

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Kinetics of the Unimolecular Dissociation of Gaseous Ethyl Bromide[1]

BY ELVIN L. VERNON AND FARRINGTON DANIELS

A search for unimolecular reactions has been in progress in this Laboratory for several years. Another communication[2] describes the thermal decomposition of several organic compounds and, of these, the dissociation of ethyl bromide was selected as the reaction most promising from a theoretical standpoint. It has been subjected to further intensive study as described in this article.

In the first investigation[2] it was established, experimentally, that the reaction is

$$C_2H_5Br \rightleftharpoons C_2H_4 + HBr$$

and various ways of calculating the rate of dissociation were discussed. The course of the reaction was followed in both researches by measuring the pressure as a function of time, using glass diaphragms[3] and all-glass or all-quartz vessels, totally immersed in a lead bath. In the present investigation the measurements were carried to lower pressures for the purpose of testing recent theories of unimolecular reactions and an improved method

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[1] Further details of this investigation may be obtained from the Ph.D. thesis of Elvin L. Vernon filed in the Library of the University of Wisconsin in June, 1932.

[2] Lessig, J. *Phys. Chem.*, 36, 2325 (1932).

[3] Daniels, THIS JOURNAL, 60, 1115 (1928).

of calculation was used, The accuracy was increased by a thermostatic control, using a photoelectric cell, and by carefully testing for minute leaks before each determination.

Experimental Procedure

The thermostat consisted of an insulated iron box containing well-stirred, molten lead.[2] Considerable elasticity in the arrangement of heaters was necessary in order to insure fine temperature control over a wide range and to eliminate wasted heat in external resistances. Only a small amount of current passed through the intermittent heater, the main heating being produced by various series and parallel combinations of seven independent coils controlled by twelve switches Each unit comprised 16 ohms in the form of a helix of No. 18 nichrome wire wound around the inside of the "transite" box and covered with "alundum" cement. With this arrangement, twenty-three different switch combinations were used to give graded inputs of energy ranging from 112 to 1300 watts with a minimum current (never exceeding 4.5 amp.) through any one heater.

The temperature was determined and maintained constant with a platinum resistance thermometer and precision bridge. A photoelectric cell was set behind a narrow slit at the zero point of the galvanometer. A beam of light from a 500-watt projection lamp was reflected from the mirror of the galvanometer and passed back and forth across the cell as the temperature of the bath rose and fell. It controlled the intermittent heater through a two-stage amplifier (71A and 01A tubes) and a sensitive relay which operated a special switch. This switch was designed to offset the time lag in the controlling apparatus by closing the heating circuit only on alternate excitations It was arranged with a spring contact pressing against a brass tilting arm which was snapped back and forth with each pull of the relay armature. Careful balancing with springs and a counterpoise was necessary. One side of the tilting arm had an insert of hard rubber which interrupted the heating circuit. As the thermostat heated up and the galvanometer beam reached the zero point the armature of the

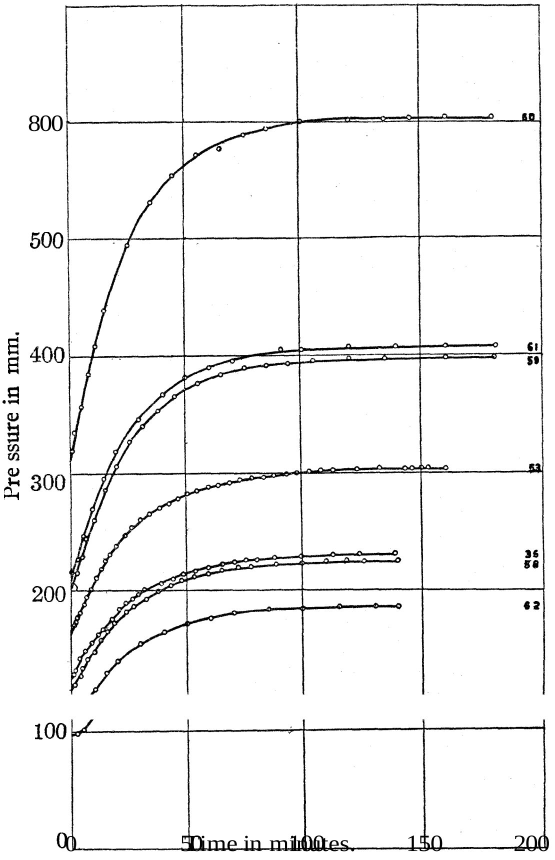

Fig. 1.—High pressure, 395°.

relay snapped the arm over to the non-conducting side and turned off the heating current. As it swung past the cell, the armature was released but the contact point still remained on the insulated side of the arm. As the bath cooled the galvanometer beam swung back to the photoelectric cell, thereby pulling the armature and snapping the switch to the conducting side and starting the intermittent heater. When it passed beyond the cell, on the opposite side, the armature was released but the switch was still on the conducting arm. The current remained on until the galvanometer beam swung across the photoelectric cell the third (and fifth, seventh, etc.) time. Temperature plotted against time gave a curve similar to a sine wave but after the control was in operation for half an hour the total fluctuation was less than 0.3". The large cooling effect produced by placing a cold body in the bath was nearly eliminated by introducing the object at a time when the heating current had just been turned off.

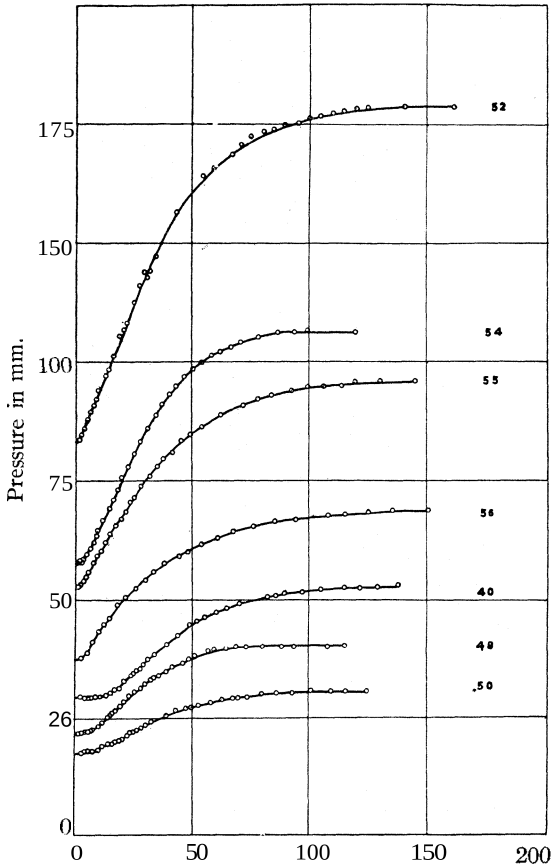

Fig. 2.—Low pressure, 395°.

The flasks and tubes were thoroughly cleaned and rendered free from carbon by heating to redness when filled with oxygen or by boiling with fuming nitric acid and rinsing with distilled water After cleaning and testing for leaks the 250-cc. Pyrex flask was lowered into position in the lead bath and the zero point of the diaphragm was taken. It was then raised into the cavity above the bath and the side arm was drawn down. The liquid ethyl bromide was previously sealed off under vacuum in a small bulb provided with a capillary tube. A short T-tube with rubber connections was so arranged that the flask could be evacuated while the capillary from the bulb extended well into the side arm of the flask. A wad of asbestos fibers in the connection to the vacuum line filtered out any particles that might be swept into the flask. The flask and newly made connections were tested for leaks with the Tesla coil and when the vacuum was satisfactory the vacuum line was closed off and the tip of the capillary broken. The liquid vaporized at once, the side arm was sealed off and the vessel lowered immediately into position in the lead bath. Pressure readings were then taken. At the end of an experiment the vessel was removed, a rubber tube was placed over the sealed-off tip of the side arm and connected to the vacuum pump. Thus when the flask was opened there was no sudden inward pressure to break the sensitive diaphragm.

The zero point changed with temperature in a specific manner for each diaphragm. In a typical case a zero point of 39 mm. was obtained (*i.* e., the manometer side of the diaphragm required **39** mm. more air pressure than the vessel side in order to make electrical contact) at 395°. At 300° the zero point was **52** and when reimmersed in the lead bath at 395° the zero point returned to **39** mm., within one and a half minutes A newly made diaphragm usually showed a slow drift for the first hour in the thermostat but then remained constant for the rest of its life. When the flask was sealed off with **83** mm. of air and immersed in the bath, about five minutes was required to reach a constant pressure with thermal equilibrium in both vessel and lead bath. The first minute and a half was further complicated with changes in the zero point.

It was found[2] that impurities seriously affected the rate of dissociation and so the final measurements, including all those reported here, were made with ethyl bromide purified in the laboratory of Professor Timmermans[4] at Brussels.

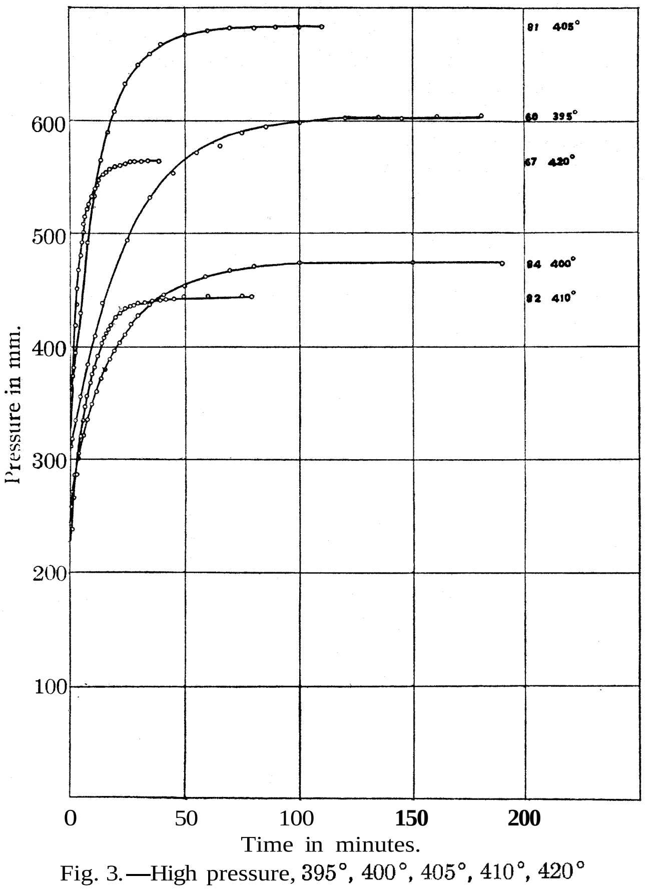

Fig. 3.—High pressure, 395°, 400°, 405°, 410°, 420°

Tests

It was necessary to exclude every trace of air because oxygen greatly accelerates the decomposition. In one case 10 mm. of air nearly doubled the rate and in another

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[4] Timmermans and Martin. J *chim. phys.*, **23, 768** (1926). **A few purified organic liquids from Professor Timmermans' laboratorv may be obtained through the U.** *S.* **Bureau of Standards.**

case 2 mm. of air had no additional effect on the final pressure but increased the rate markedly. Parallel experiments at 395" with an empty Pyrex flask and with the same vessel containing a considerable quantity of powdered Pyrex glass gave unimolecular constants of 5.90×10^{-4} and 5.88×10^{-4}, respectively. The close agreement shows that the large excess of glass surface does not affect the reaction rate The reverse reaction, the combination of ethylene and hydrobromic acid, had apparently become homogeneous, also, at this temperature, for in both cases the constants (calculated as shown later) are approximately 3×10^{-7} sec.$^{-1}$.

It was necessary to have the reaction vessels scrupulously cleaned as already described. If a vessel is allowed to stand in the thermostat for several hours after the reaction is finished, a film of carbon can be seen on the vessel walls. Presumably this film is caused by the decomposition of ethylene into carbon and hydrogen. In all the experiments recorded here the reaction vessel was thoroughly cleaned at the beginning of an experiment and this effect did not start until after the reaction was practically complete. In slow reactions at low temperatures, however, this secondary reaction was sometimes appreciable, but the final pressure was not required in the calculations. When a vessel was not cleaned and a film of carbon from a previous experiment was present, a sudden rise of perhaps 10 mm. in ten minutes was noted after the pressure had nearly reached a stationary value and the curve was nearly flat. Adsorption of gas by the original carbon film and dissociation of one molecule of ethylene into two molecules of hydrogen and solid carbon were probably involved.

Experimental Results

The experimental data are shown in Figs. 1–3 and in Table I.

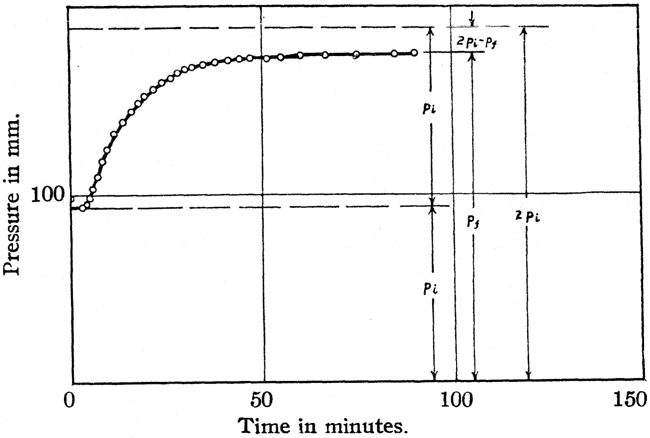
TABLE I

PRESSURE-TIME DATA INTERPOLATED FROM LARGE GRAPHS

	Temperature 395° at minutes								
Expt.	**0**	**5**	**10**	**15**	**20**	**40**	**50**	**100**	**15**
62	98	100	115	127	138	164	171	184	185
53	162	185	207	224	239	271	281	300	303
61	212	237	269	294	317	367	380	405	408
60	309	360	400	421	469	542	562	597	602
50	17.5	17.5	18.2	19.4	20.6	25.4	27.2	30.2	
40	24.1	24.1	24.2	25.2	27.0	35.6	39.5	46.8	
55	52	55.0	59.5	63.8	67.5	80.4	84.7	94.7	
52	83	86.8	93.3	99.6	105.9	127.6	135	156	
	Temperature 405°								
80	94.1	100	125	142	155	172	174		
73	234.3	293	347	381	404	445	452	458	
81	364	438	521	581	609	664	674	683	
86	18–18.5		19.8	21.6	23.5	27.5	27.8		
74	40	49.7	57.2	62.8	67.7	75.2	76.7		
87	67.1	77.5	90.3	100.4	108.6	118.8	119.9		
	Temperature 420°								
66	12.5–13	14.2	17.9	19.3	20.0	20.1			
68	34	41.7	51.7	55.4	56.9	57.6			
63	57.5	72.5	87.3	93.1	96.8	98.8			
64	89	116.7	140.3	156.0	162.7	168.1			

Calculations

The following terms are used in the calculations: p_i = initial pressure, p_f = final pressure, p_t = pressure at any time, t, in minutes, a = initial concentration of ethyl bromide proportional to p_i, and $x = p_t - p_i$ = amount of ethyl bromide decomposed in time t. $p_f - p_t$ would give the partial pressure of ethyl bromide at any time if the reverse reaction was negligible and the final pressure was exactly twice the initial pressure.



$2p_i - p_f = p_{\mathrm{EtBr}}$. $p_f - p_i = p_{\mathrm{HBr}} = p_{C_2H_4}$.

Fig. 4.—Pressure relations at equilibrium.

From Fig. 4 it is evident that at equilibrium $2p_i - p_f = p_{C_2H_5Br}$ and $p_f - p_i = p_{\mathrm{HBr}} = p_{C_2H_4}$. k_1 = rate constant for the reaction $C_2H_5Br \longrightarrow C_2H_4 + HBr$, k_2 = rate constant for the reverse reaction $C_2H_4 + HBr \longrightarrow C_2H_5Br$. K = equilibrium constant $= \frac{k_1}{k_2} = \frac{p_{C_2H_4}\,p_{\mathrm{HBr}}}{p_{C_2H_5Br}} = \frac{(p_f - p_i)^2}{2p_i - p_f}$.

When log $(p_f - p_t)$ was plotted against t, it was shown[2] that excellent straight lines are obtained out to nearly 90% dissociation. Some of the data of the present investigation are plotted in this way in the dotted lines of Fig. 5. Ordinarily these straight lines would be taken as proof that the reaction is of the first order and that k_1 is equal to the slope of the line multiplied by 2.303. As shown before[2] the rate constants calculated in this manner are too high by about 20% and they show an abnormal dependence on pressure because they do not allow for the reverse reaction.

Allowing for the reverse reaction, which is bimolecular, the differential equation is

$$\mathrm{d}x/\mathrm{d}t = k_1\,(a - x) - k_2x^2 = k_1\,(a - x) - \frac{k_1}{Kx^2} \qquad (1)$$

and integrating and evaluating the integration constant by setting $x = 0$ when $t = 0$

$$k_1 = \frac{2.303}{t\sqrt{\frac{4a}{K}+1}} \log \frac{\left(\frac{2x}{K}+1+\sqrt{\frac{4a}{K}+1}\right)\left(-1+\sqrt{\frac{4a}{K}+1}\right)}{\left(-\frac{2x}{K}-1+\sqrt{\frac{4a}{K}+1}\right)\left(1+\sqrt{\frac{4a}{K}+1}\right)} \tag{2}$$

K can be calculated from the initial and final pressures as shown and theoretically this method should be entirely satisfactory. Practically, however, the use of K is uncertain at low pressures and the accuracy is low because slight errors in finding p_i by extrapolation prevent exact calculation of K. Equation (2) is extremely sensitive to slight variations in p_i.

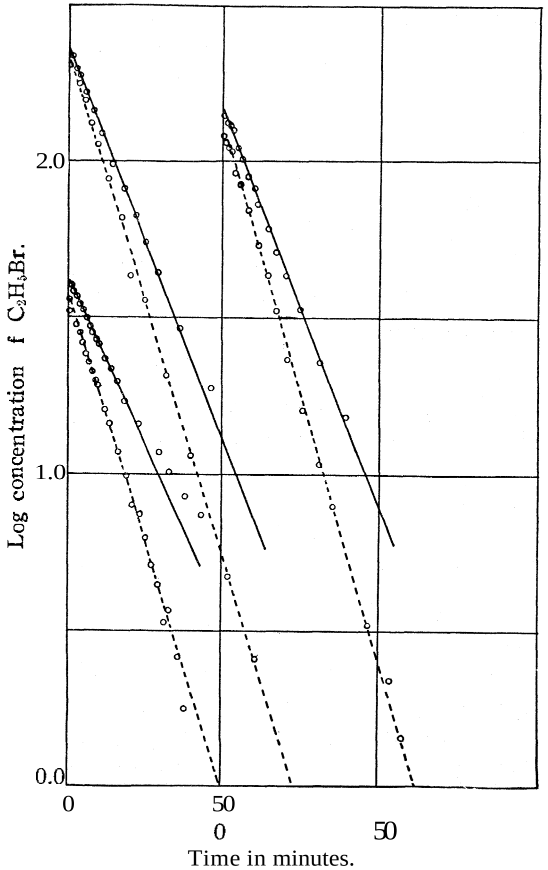


Fig 5.—*Graphs* showing first *order* reaction: full line, log $(2p_i - p_t)$; *broken* line, log $(p_f - p_t)$.

A more accurate method was devised in which the slope

$$dp/dt = \frac{d(p_t - p_i)}{dt} = dx/dt$$

of the pressure–time curves (Figs. 1–3) was measured graphically at several different times and the true values of k_1 and k_2 solved by least squares in the equation

$$\frac{1}{a-x}\frac{dx}{dt} = k_1 - k_2\frac{x^2}{a-x} \tag{3}$$

This method is quite satisfactory except at high temperatures or very low pressures where the curve becomes too flat to permit an accurate determination of dp/dt. It gives also a check on the accuracy of the extrapolated value of p_i since the reverse reaction rate k_2 is very sensitive to slight changes in the initial pressure while k_1 is comparatively insensitive under the conditions of these experiments. When the value of the initial pressure is taken too low k_2 becomes negative and since a negative value is physically absurd, a lower limit to the extrapolated value is thus obtained.

A fourth method for calculating k_1 consists in measuring the slope of the straight portion of the graph in which log $(2p_i - p_t)$ is plotted against t. This method is based on the assumption that the reverse reaction is negligible at first and that the reaction starts as if it were going to a final pressure equal to twice the initial pressure. Toward the end of the dissociation a large error is produced by assuming that the final pressure is twice the initial pressure. This method does not involve the use of p_f. In Fig. 5 it is seen that the steeper lines log $(p_f - p_t)$ fit the experimental points excellently well but in spite of this fact the less steep lines log $(2p_i - p_t)$ are more nearly correct even though the points deviate greatly from a straight line in the latter half of the reaction. This fourth method is less accurate than the third, based on the differential method, but it can be used in cases where equation **(3)** cannot be used, and it is much simpler.

A comparison of the results obtained with the four different methods is shown in Table II for three different experiments to which all the methods could be easily applied.

TABLE II

COMPARISON OF FOUR DIFFERENT METHODS OF CALCULATING k

$k \times 10^4$ sec.$^{-1}$ (395°)

Expt	p_i	p_f	I $\ln(p_f - p_t)$ *vs.* t	II Eq. (2)	III Eq. **(3)**	IV $\ln(2p_i - p_t)$ *vs.* t
53	162	303.3	6.75	4.3	5.82	5.70
52	83	153.2	6.18	4.0	5.33	5.29
55	52	95.8	5.08	4.2	4.68	4.73

The close agreement between the independent methods **3** and 4 gives confidence in their validity.

In Table III are given the results of three groups of experiments at different temperatures over a fairly wide pressure range calculated by

TABLE III

CALCULATIONS OF k

395°. $k_\infty = 5.92 \times 10^{-4}$				405°. $k_\infty = 11.1 \times 10^{-4}$				420°. $k_\infty = 25.0 \times 10^{-4}$			
Expt	p_i mm	k × 10^4	k/k_∞	*Expt.*	Pi mm.	$k \times 10^4$	k/k_∞	*Expt.*	Pi mm.	$k \times 10^4$	k/k_∞
60	309	5 98	1 010	81	364	11.19	1.011	67	308	25.0	1.000
61	212	5 88	0 994	73	234.3	11.23	1.014	64	89	20.8	0.833
59	203	5 90	996	72	139	10.85	0.980	70	63	17.2	.690
53	162	5 70	.962	80	94.1	11.02	.995	63	57.5	16.0	.640
36	123	5 60	946	87	67.1	9.02	.815	69	45	13.8	.552
58	116	5 82	984	83	41.7	7.15	.646	68	**34**	12.5	.500
62	98	5 66	956	74	40	6.98	.631	63	23	10.3	.413
52	83	5 29	.893	76	21.7	3.88	.350		24	11.7	.467
54	57 5	4 87	822			3.67	.422	66	12.5	10.8	.433
55	52	4 73	799	86	18	3.04	.274		13	11.7	.467
56	37 4	4 20	710		18.5	3.00	.361			400°	
40	24 1	3 50	592					84	247	7.67	
48	21 7	3 28	554							410°	
50	17 5	2 76	465					82	242	15.3	

method IV or method III. The specific reaction rate k refers to k_1, the corrected forward reaction expressed in sec.$^{-1}$, and k_∞ refers to the average of the high pressure values of k, where k is independent of the pressure.

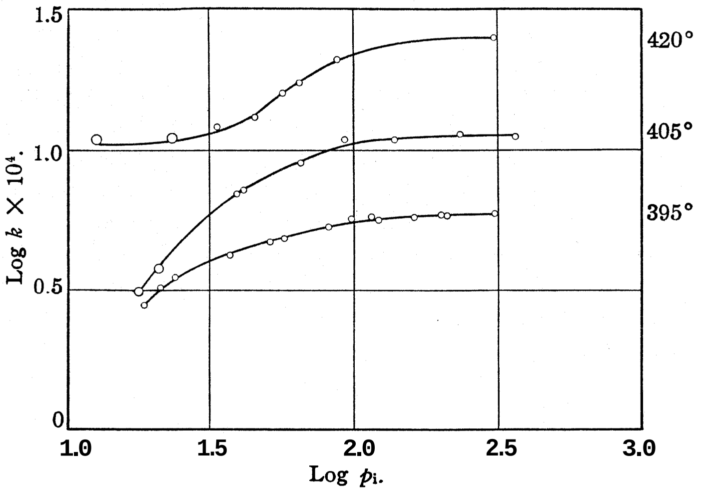


Fig. 6.—Influence of pressure on specific rate, k.

In Fig. 6 log $(k \times 10^4)$ is plotted against log p_i. For higher pressures the rate is independent of pressure. No falling off is observed down to initial pressures in the neighborhood of **125** mm. At **90** mm. and below, the decrease in k is noticeable. With this decrease there is also a tendency for the reaction to follow the second order equation rather than the first order. In Fig. 7 the reciprocal of the concentration of ethyl bromide $(1/(2p_i - p_t))$ is plotted against time for the first third of the reaction in the case of a few experiments in which p_i is about 35 mm. Under these conditions where the reaction is not complicated by the reverse reaction and where the pressure is well below the first order region the straight lines show that the second-order formula is being followed.

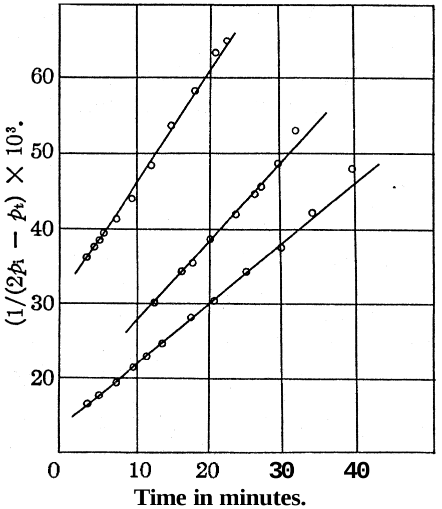


Fig. 7.—Graphs at low pressure (35 mm.) showing second order reaction: reciprocal of concentration *vs.* time.

The influence of temperature on the normal dissociation rate at high pressures is shown in curve I of Fig. 8 where log $k_\infty \times 10^4$ is plotted against $1/T$. The slope of this straight line, obtained by the method of least squares, gives a heat of activation E of 54,800 calories per mole

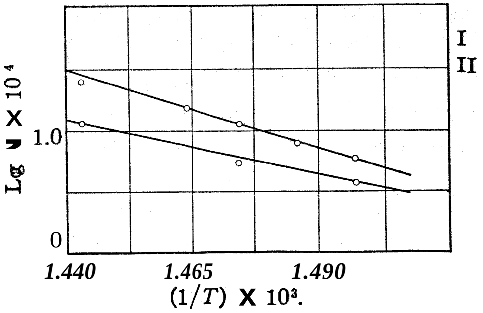


Fig. 8.—Influence of temperature on specific rate: log k vs. $1/T$; I, high pressure; II, low pressure (35 mm).

From this value is calculated the value of s in the equation

$$k_\infty = se^{-E/RT} \qquad (4)$$

as shown in Table IV.

These facts are summarized by the equation

$$k_\infty = 3.85 \times 10^{14} e^{-54{,}800/RT} \qquad (5)$$

or

$$\ln k, = 33.58 - 54{,}800/RT \qquad (6)$$

Curve II in Fig. 8 represents the data at low pressures ($p_i = 35$ mm.) and the slope of this line gives a heat of activation of 43,000 calories per mole for the low pressure or second order region.

TABLE IV

CALCULATION OF s

$T°$	668	673	678	683	693
$s \times 10^{-14}$	3.86	3.67	3.93	4.07	3.71

Theoretical Discussion

The values of E and s just given are of the same magnitude as those obtained for the other fifteen unimolecular reactions already known.[5] The value of E/RT for a given value of k falls in line with the approximately constant value found in many of the unimolecular reactions.

The theoretical treatment of unimolecular reactions and the falling off of the rate constant k at low pressures has been fully covered elsewhere.[6] Collision theories offer the best explanation of unimolecular reactions. The collision theories known as Theory I,[7,8] Theory 11[8] and Theory 111[9] have been widely discussed and it is worth while to test them with the data of the present investigation.

According to Theory I the chance of an activated molecule decomposing does not depend on the excess of energy over the critical energy ϵ_0 and it does not depend on the location of the energy within the molecule. The specific decomposition rate at any pressure is given by equation (7)

$$k = \frac{k_\infty}{1 + (\beta_1/p_i)} \qquad (7)$$

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(5) (a) Ramsperger, *Chem. Reo.*, 10, 27 (1932). (b) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, Chap. X.

(6) Reference 5b, Chapters V and X.

(7) Hinshelwood, Proc. Roy. *Soc.* (London), A113, 230 (1927).

(8) Rice and Ramsperger, THIS JOURNAL, 49, 1617 (1927).

(9) Kassel, J. *Phys. Chcm.*, 32, 225 (1928).

or

$$\log \frac{k}{k_\infty} = \log p_i - \log (p_i + \beta_1) \tag{8}$$

where β_1 depends on collision frequency and the complexity of the molecule.[10] These equations may be tested by plotting log k/k_∞ against log p as shown in Fig. 9 for the data at 395°. The theoretical curve calculated from equation (8) is shown by the curved line. The agreement between the two is not such as to support Theory I but a definite conclusion is not possible because considerable leeway is allowable in shifting the calculated curve.

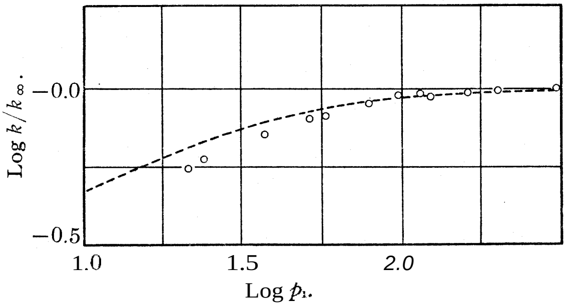

Fig. 9.—Test of equation (8).

In calculating this curve the best value of β_1 was found to be about 45 mm. ϵ_0 was calculated from the equation

$$\frac{d \ln k_\infty}{dT} = \frac{\epsilon_0 - \frac{n-2}{2}kT}{kT^2} = \frac{U_1}{kT^2} \tag{9}$$

If the molecular diameter is taken as 6×10^{-8} cm. and β_1 is taken as 45, n, the number of degrees of freedom, has a value of 21.[10] If the diameter is taken as 5.5×10^{-8} cm. the best value of n is 22. U_1 is the energy of activation per molecule calculated by the simple formula of Arrhenius. k is the gas constant per molecule.

Another test seems to show that Theory I is not adequate. Writing equation (7) in the form

$$\frac{1}{k} = \frac{1}{k_\infty} + \frac{\beta_1}{k_\infty}\frac{1}{p_i} \tag{10}$$

it is seen that when $1/k$ is plotted against $1/p_i$ a straight line should be obtained with a slope of β_1/k_∞ and an intercept of $1/k_\infty$. In Fig. 10 the points represent the experimental data at 395° and the line represents the theoretical straight line obtained from the above value of β_1. If a value of β_1 is calculated from the slope of a line passing among the experimental points there is even less agreement with Theory I than that indicated in Fig. 9.

In Theory II it is assumed that the energy of activation must be localized in a particular degree of freedom, n, before the molecule will disrupt and the

[10] β_1 is used as defined by Rice and Ramsperger, THIS JOURNAL, 49, 1621, equation (5) (1927)

chance of this localization increases as the energy ϵ increases beyond the critical value ϵ_0. Theory III is quite similar except that energy is assumed to be localized in a particular bond (2 degrees of freedom). The relative merits of Theories I, and II and III as applied to a specific reaction may be judged by comparing the energy of activation at high pressures (in the first order region) with that at low pressures (in the second order region),[11] both being calculated by the simple formula of Arrhenius. As already stated there is a large difference in these quantities. The difference is evident also from an inspection of the slopes of the lines in Figs. 6 and 8. This difference shows that Theory I is not satisfactory for explaining the facts of the present investigation but that Theories II and III are in better agreement with them. The numerical value is such as to favor Theory III slightly, but the allowable variations in the factors preclude a definite decision between the two.

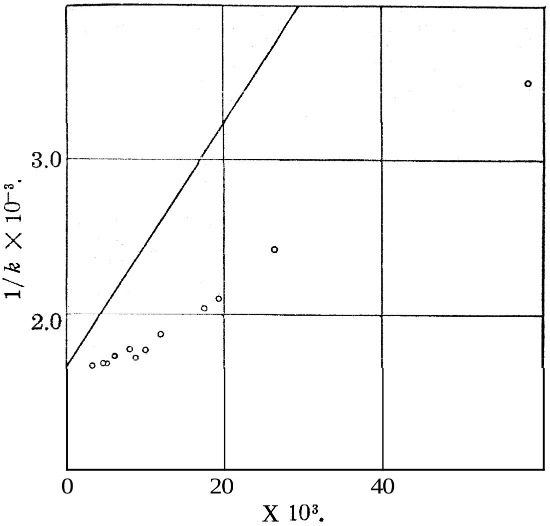

Fig. 10.—Test of equation (10).

A change in the kinetics of a reaction cannot affect the true thermodynamic equilibrium constant but it is interesting to consider possibilities with reference to an apparent equilibrium constant, calculated from partial pressures.

The present investigation offers an unusual opportunity for studying **a** reversible dissociation in which the bimolecular and unimolecular reactions proceed simultaneously. The classical equilibrium constant K is ordinarily written as

$$K = \frac{k_1}{k_2} = \frac{p_{\mathrm{HBr}}p_{\mathrm{C_2H_4}}}{p_{\mathrm{C_2H_5Br}}} \qquad (11)$$

It is shown in this investigation that k_1 decreases at low pressures. If k_2 changes in such a manner as to compensate this change in k_1 the value of K will remain constant; but if k_2 remains constant, K will decrease at low pressures. In such a case the numerical value of the ratio of the partial pressures at the right would have to decrease also at low pressures to preserve the relation indicated by equation (11).

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(11) Ramsperger, *Chem. Rev.*, **10**, 35 (1932).

Summary

1. The dissociation of gaseous ethyl bromide into ethylene and hydrobromic acid has been determined between 395 and 420° and at pressures ranging from 12 mm. to 360 mm. It is a unimolecular reaction suitable for the study of kinetics.

2. Ethyl bromide was sealed off in glass vessels totally immersed in a lead thermostat controlled by a photoelectric cell. The pressure was followed through a glass diaphragm.

3. The influence of traces of air was studied.

4. The unimolecular dissociation is accompanied by a bimolecular recombination. Four different methods for calculating the specific decomposition rate k are discussed.

5. The specific rate k starts to decrease at pressures below 100 mm. and at lower pressures the reaction tends to follow the second order equation.

6. The data above 100 mm. pressure are well expressed by the formula, $k = 3.85 \times 10^{14} e^{-54,800/RT}$

7. The data are used to test collision theories of unimolecular reactions. They do not agree well with the predictions of Theory I. The temperature coefficients at high and low pressures suggest a better agreement with Theory III or II.

8. A relay switch is described which operates only on alternate excitations.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

The Effect of an Electric Field on the Flame Temperature of Combustible Gas Mixtures[1]

BY BERNARD LEWIS[2] AND C. D. KREUTZ[3]

The effect of an electric field on the flames of a number of combustible gases has been reported on by several investigators.[4] It was found that the electric field exerted a marked influence, increasing or decreasing the speed of propagation of the flame (depending on experimental conditions), seriously deforming and weakening the appearance of the flame, and under suitable conditions eventually extinguishing it completely.

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(4) Malinowski, *J. chim. phys.*, **21**, 469 (1924); Malinowski and Lawrow, *Z. physik*, **59**, 690 (1930); Bernackyj and Retaniw, *Ukr. Physik Abhand.*, vol. II, no. 1, p. 9 (1928); F. Haber, *Sitzb. Preuss Akad. Wiss.*, 11, 162 (1929); Thornton, *Phil. Mag.*, **9**, 260 (1930); Guénault and Wheeler, *J. Chem. Soc.*, 195 (1931); Lewis, THIS JOURNAL, **53**, 1304 (1931); Muendel, Thesis, Carnegie Institute of Technology, 1931; Malinowski and Lawrow, *Phys. Z. Sowjetunion*, **2**, 52 (1932).

Mines, the Carnegie Institute of Technology, and the Mining Advisory Board, the present work was undertaken to determine what effect, if any, the electric field had on the flame temperature. In all cases investigated a lowering of the flame temperature was observed to a more or less degree, which depended on the composition of the gas mixture and certain mechanical details described below.

Method and Procedure

The sodium line reversal method was used for determining flame temperatures. The same apparatus was employed as in previous investigations.[5] The method of applying a high direct potential was the same as reported previously.[4]

The burner consisted of **32** porcelain tubes (*ca.* 3-mm. bore) closely packed together and cemented gas-tight into the opening of a small brass box 5.5 by *3.5* cm. similar to those described in Fig. *2* of the paper by Jones, Lewis, Friauf and Perrott.[5] To meet the requirements of faster or slower burning mixtures, tubes of smaller or larger bore could be substituted. The electrodes consisted of two brass plates 6 cm. square containing a hole 8 mm. in diameter, two-thirds the distance up, through which the light beam, essential in the line reversal method, passed. The electrodes were mounted on porcelain rods which were attached to the brass box and which were movable up or down with respect to the burner tips. Observations could therefore be made at different heights of the flame, exposing more or less of the latter to the action of the field. The electric field was applied across the flame—*i. e.*, in the direction of the light beam. Thus, if the flame was distorted by the field it was not displaced from the axis of the light beam. To prevent the flame from touching the negative electrode toward which it was pulled when the field was applied, this electrode was placed **1.5** cm. farther from the center of the group of burner tips than the positive electrode. In this way cooling by contact with the electrode was eliminated. The over-all distance between the electrodes was 6 cm., while the diameter across the burner tips was **2.5** cm. Care was taken to ensure that the flame did not touch the electrode below the point of observation. Above the point of observation the flame sometimes approached the electrode sufficiently close to allow thin sparks to pass between it and the flame boundary. Readings were not taken under these conditions, but the potential was lowered to avoid this. Temperature readings with the electric field were sandwiched between readings without the field. The potential could be varied up to about 18,000 volts.

The combustible gases used were Pittsburgh natural gas, ethylene, isobutane and butylene mixed with air. Three mixtures were used for each gas, one giving approximately a maximum flame temperature (close to theoretical oxygen content), and the others rich and lean mixtures. For the first mixture, readings were made at intervals of 1 cm. from **0.5** cm. to 6.5 cm. above the burner tips. For the rich and lean mixtures observations were made only at **6.5** cm. Gas samples were collected and analyzed on a Bone–Wheeler apparatus.

Finally some observations were made of the effect of an electric field on a very low-temperature and a high-temperature flame of carbon disulfide vapor.

Results

A summary of the results is given in Table I and illustrated in Fig. 1. The curves in the figure are for the approximately maximum temperature mixtures. An effect of less than 9° is ignored.

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(5) Loomis and Perrott, Ind. *Eng. Chem.*, 20, 1004 (1928); Jones, Lewis, Friauf and Perrott, THIS JOURNAL, 53, 869 (1931); Jones, Lewis and Seaman, *ibid.*, 53, 3992 (1931); 54, 2166 (1932).

TABLE I

SUMMARY OF RESULTS OF EFFECT OF ELECTRIC FIELD ON FLAME TEMPERATURES

	Flame temperatures															
	Natural gas				Ethylene				Isobutane				Butylene			
Height above burner, cm.	Per cent. of gas	No field, °C.	With field, °C.	ΔT	Per cent. of gas	No field, °C.	With field, °C.	ΔT	Per cent. of gas	No field, °C.	With field, °C.	ΔT	Per cent. of gas	No field, °C.	With field, °C.	ΔT
0.5	9.06	1775	1772	..	6.95	1923	1916	...	3.59	1802	1802	..	3.93	1844	1842	..
1.5	9.06	1851	1848	..	6.95	1966	1942	24	3.59	1851	1841	10	3.93	1864	1862	..
2.5	9.06	1835	1828	..	6.95	1966	1950	16	3.59	1848	1838	10	3.93	1848	1842	..
3.5	9.06	1809	1794	15	6.95	1933	1924	9	3.59	1844	1828	16	3.93	1848	1848	..
4.5	9.06	1770	1752	18	6.95	1912	1892	20	3.59	1821	1812	9	3.93	1843	1832	11
5.5	9.06	1756	1725	31	6.95	1919	1900	19	3.59	1802	1764	38	3.93	1832	1806	26
6.5	9.06	1737	1686	51	6.95	1868	1780	88	3.59	1782	1743	39	3.93	1811	1776	35
6.5	7.15 (lean)	1649	1597	52	4.67 (lean)	1595	1479	116	1.85 (lean)	1712	1647	65	3.82 (lean)	1811	1760	51
6.5	10.0 (rich)	1739	1718	21	10.98 (rich)	1830	1818	12	3.92 (rich)	1733	1710	23	5.0 (rich)	1742	1735	..

It is observed that the lowering of the flame temperature increases as more of the flame is exposed to the field below the point of observation. One would expect, therefore, that the effect would be lessened if the gases were exposed to the field for a shorter time. This was found to be the case when an ethylene mixture was passed through the burner with a greater velocity. A mixture deficient in oxygen was not used for butylene.

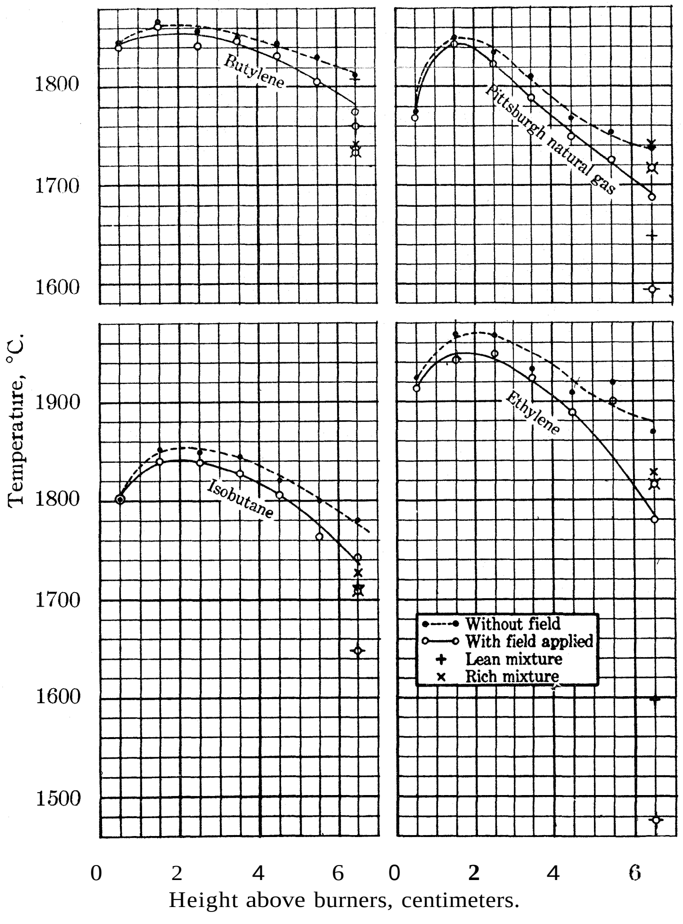

Fig 1 —Effect of electric field on flame temperatures.

There is a remarkable difference between the effects on rich and lean mixtures. In all cases the effect is small for rich mixtures but large for lean mixtures. Thus, for example, the temperature lowering for ethylene is 12° for a rich and 116° for a lean mixture.

The authors wish to present the experimental facts but are not disposed to discuss the meaning of the results at the present stage of progress.

It was of interest to see whether a low-temperature flame could in any way be affected or distorted by the electric field. A stream of carbon disulfide vapor was passed through the burner. The air necessary for combustion was picked up after leaving the burner tips. The resulting flame had a temperature of the order of 100°. The amount of ionization in such a flame is negligible. The flame was unaffected by a high electric field. However, a high-temperature flame of carbon disulfide (about 1600–1700°), produced by premixing the air in which there is probably a considerable amount of ionization, was affected as other high-temperature flames are. Readings of the temperature-lowering effect of the field in the latter flame were unreliable due to inconstancy of the mixture under the present arrangement.

Summary

The effect of an electric field applied transversely across a flame, on the flame temperatures of rich, lean and nearly theoretical mixtures of Pittsburgh natural gas, ethylene, isobutane and butylene in air was investigated using the sodium line reversal method for measuring their flame temperatures. In all cases investigated the effect of the field was to reduce the flame temperature. This was greatest the slower the gas velocity and the greater the length of flame which was exposed to the field before observations were made. The greatest effect was found for lean mixtures and the smallest for rich mixtures. Thus, for ethylene the temperature lowering for a lean mixture was 116° and for a rich mixture 12°.

It was shown that a low-temperature flame of carbon disulfide vapor is unaffected by an electric field but that a high-temperature flame of the same combustible vapor is deflected toward the negative electrode as are the flames of other combustibles.

PITTSBURGH, PENNSYLVANIA

RECEIVED AUGUST 15, 1932
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

The Absorption Spectra of Cobaltous Compounds. IV. The Alkali Oxide–Boric Oxide Glasses

BY WALLACE R. BRODE

A spectroscopic examination of commercial samples of blue cobalt glasses shows that their absorption spectra are by no means identical (Fig. 1) This fact has been noted in the literature,[1,2,3] but, beyond the inference that the constitution of the glass will determine the characteristics of the absorption spectra, there are very few specific data on the cause of the blue color in cobalt glasses and glazes or the reasons why their absorption spectra will give bands with different relative intensities.

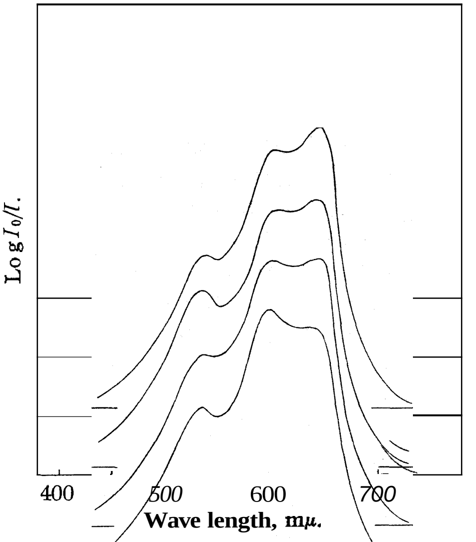

Fig. 1.—The absorption spectra of four typical samples of blue cobalt glasses. The upper curve is characteristic of potash glasses while the lower curve is characteristic of soda glasses.

Since even the simplest of the commercial glasses contain the oxides of many elements it was felt best to avoid such combinations and confine the preliminary experiments to two component systems, in an attempt to determine the effective component and the nature of the cobalt complex that produced the color. As might have been predicted the two component systems had a marked tendency to form crystalline compounds instead of amorphous glasses. In time it is hoped that a large series of basic oxide–acidic oxide glasses can be studied, including systems with more than two component compounds and the substitution of oxygen with halogens, sulfur or other elements. The system chosen for the preliminary study of cobalt colored glasses was that of the alkali oxides with boric oxide. This system includes the borax bead which is used in the qualitative detection of cobalt.

A study of the absorption spectra of cobaltous hydroxide, dissolved in concentrated aqueous alkali hydroxide solutions, by Dr. R. A. Morton and

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(1) Fedotieff, *Z. anorg. allgem. Chem.*, **134**, 87 (1924).

(2) Zsigmondy, *Ann. Physik*, 4, **60** (1901).

(3) Gibson and co-workers, Technologic Papers of the Bur. Standards, No. **148** (1920), Scientific Papers of the Bur. Standards, No. **547** (1927).

the author[4] at the University of Liverpool, showed that a slight change in intensity of the absorption bands, without a change in wave length, would be expected with a change from NaOH to KOH. The data presented in this paper would confirm this effect and indicate that the cobalt color in concentrated aqueous alkali hydroxide is the same as in the alkali oxide glasses.

In earlier papers of this series[6] it has been shown that a change from Cl, to Br, to I in the complex causes a marked increase in wave length of the absorption band with an increase in the molecular weight. The conclusion was drawn that these elements must be directly connected with the chromophore, since their mass influences the frequency of vibration of the chromophoric group. In this paper a new type of effect is described, in which the change in elements, from Li to Na to K to Cs, causes no shift in the frequency of the band but rather a change in the band intensities. This latter effect is not of necessity due to a difference in mass and might arise from certain chemical differences such as a tendency to form polyvalent compounds, electromotive effects, etc. It would seem then that none of these alkali metals are directly connected to the chromophore yet they have a close relation with the cobalt such as might occur in a coordinated oxide formed from M_2O and CoO in which the metal would not be directly attached to the cobalt but its affinity for oxygen would determine the ease of formation of the coordinated cobalt oxide and the strain upon the cobalt–oxygen coupling. Such a theory would lead to the prediction of an easily formed and stable cobalt oxygen coordinated complex in the presence of Cs_2O and a difficultly formed and unstable complex with Li_2O. The experimental data in this paper are in accord with this theory.

In an earlier paper[5b] it was shown that the addition of halogen acids to a neutral pink solution of a cobaltous salt converted it to a blue-green solution. In this paper it is shown that the addition of alkali oxides to a pink cobalt glass of boric oxide converts the color to blue. These different absorption spectra should not be considered as derived from extreme acid and basic colors with the pink cobaltous colors as the neutral range. It is possible to add halogen salts to a blue cobalt glass and change the absorption bands to the blue-green system of the halogen acids without passing through any pink stage. It has been previously shown[5c] that a similar effect is observed with regard to the change from the blue pyridine–quinoline solutions to the halogen acid solutions. Strong acids such as sulfuric acid and nitric acid do not give blue solutions while neutral solvents such as ethyl alcohol, ethyl ether and acetone give blue solutions. The evidence points to an oxide coordinated system which differs only from the halogen system by replacement of the halogen with oxygen. The similarity of the

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(4) Then a Fellow of the John Simon Guggenheim Memorial Foundation.

(5) (a) Brode, *Proc. Roy. Soc.*, **118A, 286 (1928)**; (b) Brode and Morton, ibid., **120A, 21 (1928)**; (c) Brode, THIS JOURNAL, **53, 2457 (1931)**.

two systems is shown through the analogous shape of their absorption bands, the oxygen-system bands being of similar shape but shifted to a higher frequency, which would be expected as a result of the smaller mass of the oxygen as compared with the halogens, Cl, Br and I. In both the oxygen and halogen systems the colors can be shifted from pink to blue by an increase in temperature. The pink colors obtained are the same in all systems, while the blue colors vary depending on whether O, Cl, Br, I, S, SCN, pyridine, quinoline, etc., are combined with the cobalt.

In the alkali oxide–boric oxide glasses two different influences are considered, (a) the change in the ratio between the alkali oxide and boric oxide concentrations, and (b) the change of the alkali oxide from Li to Na, to K to Cs. Since pure boric oxide alone gave only the pink color, characteristic of the uncoordinated cobaltous compounds, it was felt that its action, like that of water in the halogen acid systems, was merely that of a solvent. There is another possible type of substitution in this series of glasses which should be quite convincing in showing which of the elements involved actually coordinate with the cobalt. This would involve the replacement of oxygen with other elements such as the halogens, sulfur, selenium and tellurium. Although glasses of this type will be discussed in a subsequent paper, the Na_2S–$2B_2S_3$ (thioborax) glass has already been prepared and the shifted position of the bands definitely confirms the theory that oxygen and sulfur are coordinated with cobalt in much the same manner as the halogens.

Preparation of Glasses and Method of Observation

The melts described in this paper were prepared, in unglazed Sillimanite crucibles, by thoroughly grinding and fusing to a clear liquid the weighed quantities of alkali carbonate, boric acid and cobalt carbonate. When completely fused each melt weighed between 10 and 15 g., of which the cobalt in the form of CoO formed about 0.1%. Melts with ratios of one mole of alkali oxide to two moles of boric oxide (M_2O–$2B_2O_3$) or **lower** boric oxide content, appreciably etched the crucibles and M_2O–B_2O_3 melts invariably went through the crucible in a short time. For this reason many of the glasses with a ratio of M_2O–$2.5B_2O_3$ or less boric oxide were subsequently prepared in platinum crucibles. These latter glasses gave absorption curves identical with those obtained from the glasses prepared in the Sillimanite crucibles, indicating that there was no apparent color effect due to the dissolving of small amounts of Al_2O_3 or SiO_2. All the cesium glasses were prepared in platinum crucibles.

For the absorption spectra observations, glass disks with nearly plane surfaces were prepared by the use of rings made of a single loop about 2 cm. in diameter on the end of a nichrome or platinum wire. In cases where extra thick glasses were desired two or three turns were used. A bead from the melt was formed on the wire loop of a size sufficient to produce a disk from 3 to 4 mm. thick. The disk was laid on a polished carbon block and the upper surface liquefied with a gas oxygen blow torch. The bead was then allowed to cool and when nearly solidified it was turned over and pressed lightly on the polished carbon block. The surface then uppermost was similarly treated and afterwards each was fire polished or flashed with the flame to remove slight roughness caused by the contact cooling with the carbon block The resulting glasses were quite satisfactory for the measurement of their absorption spectra. In a few cases where there was a marked tendency to crystallize it was necessary to form the disk by rapid cooling and no fire polishing was possible. The method used in such cases was to pour out a puddle of the melt on a polished stone surface and freeze it at once by pressing down on the top of this drop with a cold carbon block. All of the prepared disks were kept in an oven at 100° until observations on their absorption spectra and thickness could be made. This treatment effected a partial annealing and prevented the rapid formation of a film on the glasses due to the hydration of the boric oxide. A subsequent coating of collodion served to preserve the samples permanently.

The absorption spectra measurements were made on a Bausch and Lomb spectrophotometer. The data, in a graphic form, as presented in this paper have been recalculated to equivalent concentrations of cobalt and convenient thickness of sample. Several samples were prepared of certain alkali oxide–boric oxide melts with widely differing cobalt concentrations (varying from 0.04 to 2.5%). These gave nearly identical absorption spectra curves in thicknesses inversely proportional to the cobalt concentration and hence showed that there were no concentration effects within the ranges studied.

In the cases of those samples which could not be fire polished after pressing out, and of certain others which were partially crystallized, a necessary correction was made for the considerable diffusion and general absorption of light from the rough surfaces. This correction was made by subtracting the value of the absorption coefficient obtained at 730 $m\mu$ from all of the observed values, since it was shown in the clear samples and other glasses studied that there was no absorption at this point due to the cobalt color. Observation points have been omitted from the curves in this paper in order to permit a better visual comparison of the curves. Readings were made every 5 $m\mu$ from approximately 420 $m\mu$ to 730 $m\mu$, each plotted point being the average of several readings. Separate settings were made at each of the maxima, and additional data obtained for these points. The sample thicknesses and to some extent the concentrations increase as one goes from blue to pink glasses. The extinction coefficient for the blue glasses is about ten times that for a pink glass of the same thickness and concentration of cobalt. The solubility of cobalt oxide in boric oxide is very low so that some of this large drop in extinction coefficient may be due to a colloidal suspension of the cobaltous oxide in place of a true solution.

Discussion

Because of available data on the sodium oxide–boric oxide system the first glasses to be made were of this composition and more concentrations were considered in this series than in the subsequent alkali oxide glasses (Fig. 2). Ponomareff[6] has shown that there are eutectics in this system at $Na_2O–1.5B_2O_3$, $Na_2O–2.5B_2O_3$ and $Na_2O–3.5B_2O_3$ and that there are molecular compounds corresponding to $Na_2O–B_2O_3$, $Na_2O–2B_2O_3$, $Na_2O–3B_2O_3$ and $Na_2O–4B_2O_3$ but that beyond this last boric oxide concentration there does not appear to be a continuation of this series of eutectics and compounds. This might indicate that the maximum stable sodium borate was the octaborate, $Na_2B_8O_{13}$. In Fig. 2 it is noticeable that in this same neighborhood of $Na_2O–4B_2O_3$ the change takes place between the pink and blue glasses. This color change does not take place at a fixed concentration ratio of sodium oxide to boric oxide but rather occurs over a given concentration range. This range may be shifted to higher or

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(6) Ponomareff, *Z. anorg. Chem.*, 89, 390 (1914)

lower alkali oxide concentrations by a change in temperature. At high temperatures large amounts of boric oxide are required to produce a pink coloration, while at low temperatures, especially with liquid air, only a very small amount of boric oxide is necessary to produce a pink color. It is quite possible that a study of the stability of these various sodium oxide–boric oxide compounds at other temperatures would show a similar variation as the temperature color change. The change from pink to blue is not a shift of the frequency of the absorption band but rather the loss of intensity in one band concomitant with the gain of intensity of other bands, similar to the conditions in an indicator color change? Glasses within this equilibrium range will show these bands and hence the resultant curve should be capable of analysis into component curves, providing an intermediate is not formed.[8] Subtraction of either the extreme blue or pink curves from the equilibrium curves indicates

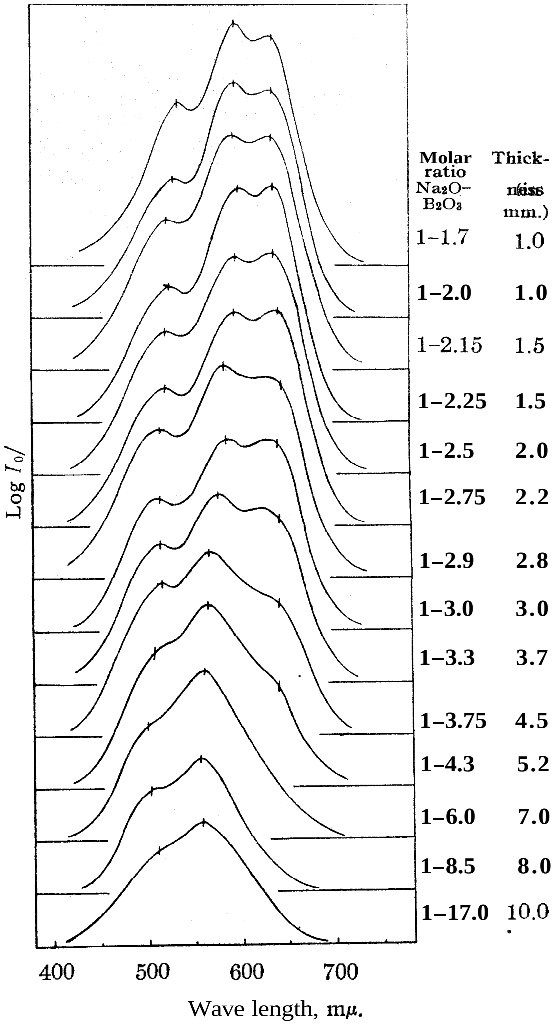

Fig. 2.—The absorption spectra of sodium oxide–boric oxide cobalt glasses. Cobalt concentration = 0.2 g. Co per 100 g. of glass. The sodium oxide–boric oxide molecular ratios and the thickness values in mm. of the samples are given to the right of the curves. It should be noted that a greater thickness or concentration of cobalt is necessary to produce an absorption band in the pink samples with an extinction coefficient of approximately the same value as in the blue samples. In order to avoid the overlapping of curves, the ordinates of each curve in this and subsequent figures in this paper have been offset 0.4 in extinction coefficient (log I_0/I) above each adjacent curve.

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(7) Brode, This Journal, **46**, 581 (1924).

(8) Brode, *Bur. Standards J. Research*, **2**, 520 (1929).

that an intermediate compound or partially coordinated complex must exist between the blue and pink colored forms. A similar intermediate compound was previously shown to exist[5] between the pyridine–quinoline blue solutions and the halogen acid blue solutions.

With an extremely low concentration of boric oxide, the band at 640 mμ drops slightly in intensity in much the same manner as has been shown in the case of certain indicators with an excess of alkali or acid concentration.

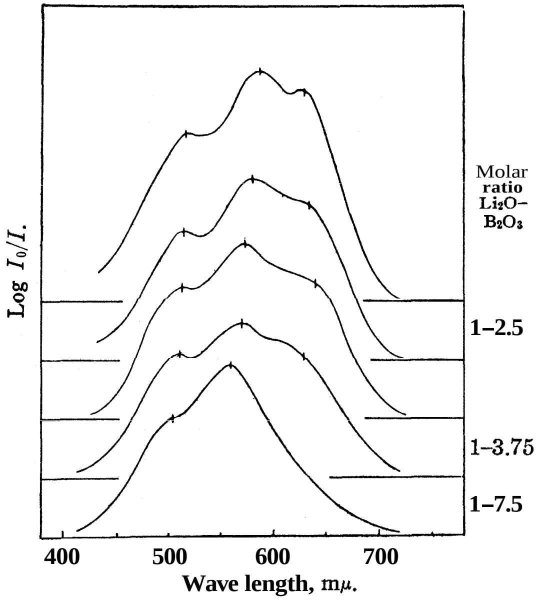

Fig. 3.—The absorption spectra of lithium oxide–boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

The data on the Li, K and Cs glasses (Figs. 3, 4 and 5) are similar to the data on the sodium glasses, although there are some progressive changes on substituting the elements in the order of their periodic arrangement. While lithium glasses have a color change point near that of the sodium glasses, the equilibrium range covers a much wider variation of concentration, so that those with the lowest amount of boric oxide are still a decided purple in color and show a considerable amount of absorption due to the pink or cobaltous color. In general the lithium glasses were high melting and had a strong tendency to crystallize. As would be predicted, the potassium glasses have apparently a smaller range of concentration variation for the color change and hence give a purer blue color with a sharper absorption band in the red than the corresponding sodium and lithium glasses. As in the case of the latter, there is a drop in the intensity of the 640 mμ band with a very low boric oxide concentration. In intermediate concentrations, however, this band is much stronger than the same band in the sodium glasses. In the blue potassium glasses there is a slight shift of the bands toward the red. This is not due to an increase in the molecular weight of the chromophore such as would occur if the potassium were directly combined with the cobalt, but rather to the smaller amount of absorption of the pink band which by its additive effect would cause an apparent shift in the wave length of the band toward the blue. If this shift had been due to an increase in molecular weight, then the bands of the cesium glasses with an atomic weight of about three times that of potassium and nearly six times that of sodium should show a marked shift, just as the shifts in the halogen–cobalt complexes from Cl, to Br, to I are in proportion to their atomic weights.[5b] There was no such shift in the cesium glasses (Fig. 5), which confirms the theory that the cobalt is not directly coordinated with the alkali metals. There is a noticeable variation of the relative intensities of the 640 mμ band in the different alkali oxide glasses. This band is relatively weak in the lithium glasses and strong in the potassium glasses. The cesium glasses indicate a still stronger band at this point but the measurements of their curves were not so accurate as the others. The melting point of (Cs_2O–$3B_2O_3$) glass was rather high and there was a marked tendency to crystallize. In addition, the cesium seemed to absorb oxygen very easily, forming the higher oxides and yielding an opaque glass. The only two satisfactory cesium glasses were the Cs_2O–$2B_2O_3$ and the Cs_2O–$2.5B_2O_3$, the latter being quite low melting.

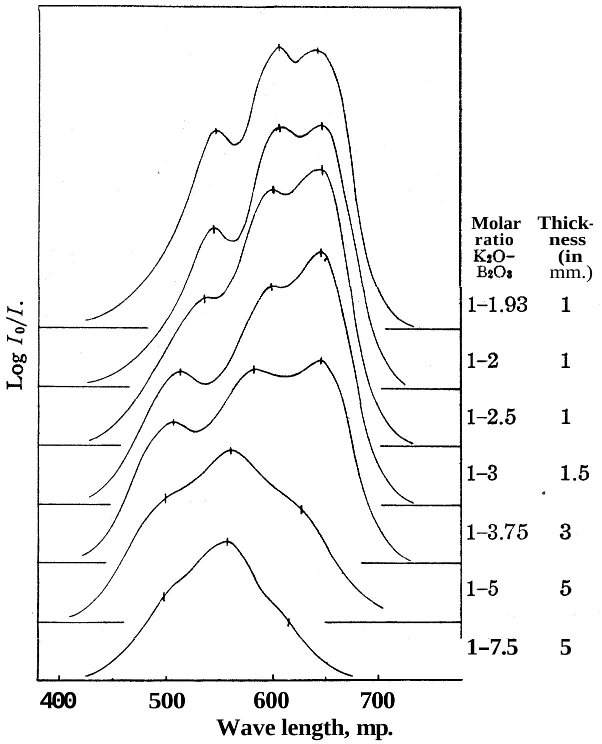

Fig. 4.—The absorption spectra of potassium oxide–boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

If the color is due to an oxide complex, similar to the quinoline halide complex, then it should be possible to convert the oxide complex to a halide complex without passing through the pink or cobaltous stage. Addition of alkali metal halides produced first a purple-gray glass with a flat broad band due to the two component band systems and a possible intermediate halogen-oxygen complex. On further addition of the alkali metal halide the halogen system with bands identical with those obtained in the concentrated halogen acids was obtained.[5b] The chloride glass was bright blue-green, the bromide glass yellow-green and the iodide glass yellow in color. Only a trace of halide was necessary to convert the pink glasses to the corresponding halogen colored glass; the intense alkali blue glasses, however, required considerable halide to convert them to the halogen colors.

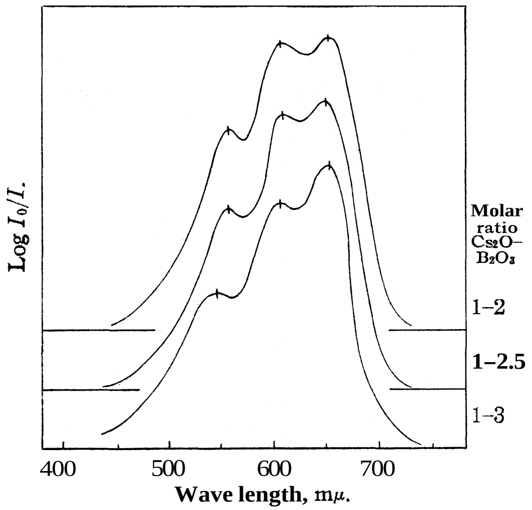

Fig. 5.—The absorption spectra of cesium oxide–boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

Summary

A spectrophotometric study has been made of the alkali oxide–boric oxide cobalt glasses. It has been shown that the position of the absorption bands in the blue glasses is unaltered by a change of alkali oxide and hence the alkali metal itself is not directly attached to or a part of the chromophore. The change of the alkali oxide to the corresponding alkali sulfide or halide produces bands which are characteristic of these complexes and whose frequency position is shifted with a change of the atomic weight of the substituting element. The cobalt oxide blue glasses therefore belong to the same system of coordinated cobalt blue compounds as the halogen acid colors, the halogen salt colors such as cobaltous chloride in the presence of calcium chloride or aluminum chloride, the alcohol, acetone, ether, and other organic blue solutions, the pyridine and quinoline–halogen complexes and the sulfur and thiocyanate colors. In all of these the coordinating element adjacent to the cobalt is apparently part of the chromophore while other elements attached to this element have little influence on the band other than an indirect effect which is apparent in the data only as modifications in the relative intensity of the bands. The pink glasses containing a high concentration of boric oxide have the same absorption band as is to be found in the water solutions of cobaltous salts or the sulfuric and acetic acid solutions and which is ascribed to the uncoördinated cobaltous atom. It is possible to prepare cobalt glasses with the proper concentration of oxides such that they will be pink at a given temperature and blue at a higher temperature. For this purpose potassium oxide is to be preferred to lithium and sodium oxides. With a given molar concentration, a more brilliant blue glass is obtained with potassium than with sodium or lithium oxides.

COLUMBUS, OHIO

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PUBLISHED MARCH 7. 1933

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, FERTILIZER AND FIXED NITROGEN INVESTIGATIONS]

The Solubility of Nitrogen in Water at 50, 75 and 100" from 25 to 1000 Atmospheres

BY R. WIEBE, V. L. GADDY AND CONRAD HEINS, JR.

There is no reliable method by which the solubilities of gases in liquids at high pressure may be calculated or predicted. Carefully compiled experimental data, therefore, become of theoretical as well as immediate practical value.

Goodman and Krase[1] measured the solubility of nitrogen in water from 100 to 300 atmospheres over a wide range of temperatures while Frolich and associates[2] obtained the solubility of nitrogen in water at 25° up to 200 atmospheres. It will be seen that there is some disagreement between the various results. The data presented here are an extension of previous work.[3]

Apparatus and Method

The apparatus and method used are somewhat similar to those described previously.[4] Fig. 1 shows the apparatus. Cylinders A and B of 1000 and 300 cc. capacity, respectively, were filled with water to three-fourths capacity. For the high pressure approach gas was bubbled through A and B successively at a pressure above the final value in order to obtain supersaturation. The pressure was then lowered to the desired level and gas was bubbled through for several hours. The gas flow was then turned off and, after standing from two to fourteen hours, samples were taken. In the low pressure approach the water was saturated at a pressure below the final value and then gas was bubbled through at the final pressure for about three hours. Samples were taken only from B. A was used as a

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(1) *Goodman and Krase, Ind. Eng. Chem.*, 23, 401 (1931).
(2) *Frolich. Tauch, Hogan and Peer, ibid*, *23*, 548 (1931).
(3) *Wiebe, Gaddy and* Heins, *ibid.*, *24*, 927 (1932).
(4) *Wiebe, Gaddy and* Heins, *ibid*, *24*, 823 (1932).

reservoir to save time in saturation. In the low pressure measuring system the 30-cc. buret C measured the volume of water while the other two burets took care of the gas sample. The water sampling buret C could be read to 0.01 cc. Pressures were read on two piston gages described by Bartlett and co-workers.[5] The nitrogen was 99.9% pure, the impurities being argon and traces of oxygen.

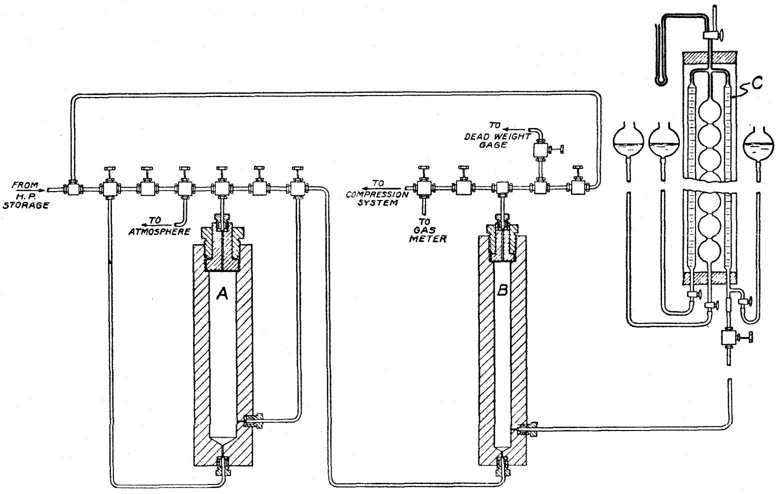

Fig. 1.

Discussion of Results

In Table I the experimental values are tabulated. The errors were calculated by means of the formula[6]

$$E = 0.6745 \pm \sqrt{\frac{\Sigma \Delta^2}{n(n-2)}}$$

and are shown in the third and fifth columns of Table I.

As will be seen, both approaches yield practically identical values, showing that equilibrium must have been reached. The final value was, therefore, obtained from an average of all observations. The absolute value may be different from the experimental by a few tenths per cent. due to the impurities and due to calibration errors of the burets and gages. The latter error will be greater at low pressures. The probable error naturally takes into account only accidental errors of observation. A slight error may also arise from the correction for the gas left in the water sample in the buret but this also becomes negligible at higher pressures.

A correction was made for the change of the partial pressure of water due to the total pressure. This correction is naturally most uncertain in the high pressure range of the 100° isotherm but in the worst case

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(5) *Bartlett,* Cupples *and Tremearne,* This journal, **50,** *1275 (1928).*

(6) Deming, *Phys. Rev., to appear.*

TABLE I

ABSORPTION COEFFICIENTS (CC. OF GAS AT S. T. P. PER G. OF WATER) OF NITROGEN IN WATER

Press of nitrogen in atm.	Number of runs for low press. approach	Av. for low press. approach	Number of runs for high press approach	Av. for high press. approach	Final values
25.00 ± 0 03° [a]					
25	10	0.348 ± 0.000	12	0.348 ± 0.000	0.348 ± 0.000
50	10	673 ± .001	10	.675 ± .001	.674 ± .001
100	10	1.262 ± .001	7	1.268 ± .001	1.264 ± .001
200	6	2.253 ± .002	6	2.260 ± .002	2.257 ± .001
300	9	3.062 ± .004	15	3.060 ± .002	3.061 ± .002
500	14	4.436 ± .002	14	4.446 ± .003	4.441 ± .002
800	8	6.133 ± .01	19	6.135 ± .00	6.134 ± .003
1000	15	7.15 ± .00	18	7.15 ± .01	7.15 ± .00
50.00 ± 0.03°					
25	9	0.273 ± 0.000	6	0.273 ± 0.000	0.273 ± 0.000
50	7	.533 ± .001	11	.533 ± .001	.533 ± .001
100	14	1.011 ± .000	5	1.011 ± .001	1.011 ± .000
200	7	1.829 ± .001	11	1.830 ± .001	1.830 ± .001
300	7	2.532 ± .001	10	2.535 ± .001	2.534 ± .001
500	5	3.718 ± .002	14	3.721 ± .002	3.720 ± .002
800	9	5.219 ± .003	7	5.223 ± .001	5.221 ± .002
1000	7	6.114 ± .006	7	6.131 ± .006	6.123 ± .005
75.00 ± 0.03°					
25	8	0.254 ± 0.000	7	0.254 ± 0.000	0.254 ± 0.000
50	7	.494 ± .000	7	.494 ± .001	.494 ± .001
100	7	.946 ± .000	8	.946 ± .000	.946 ± .000
200	8	1.732 ± .001	6	1.731 ± .001	1.732 ± .001
300	7	2.414 ± .001	5	2.412 ± .001	2.413 ± .001
500	7	3.584 ± .001	5	3.583 ± .002	3.583 ± .001
800	8	5.064 ± .002	6	5.060 ± .002	5.062 ± .001
1000	5	5.927 ± .002	5	5.939 ± .004	5.934 ± .003
100.00 ± 0.05"					
25	7	0.266 ± 0.000	9	0.265 ± 0.000	0.266 ± 0.001
50	7	.516 ± .001	7	.515 ± .001	.516 ± .001
100	7	.986 ± .001	8	.986 ± .001	.986 ± .001
200	9	1.822 ± .001	7	1.821 ± .002	1.822 ± .001
300	15	2.546 ± .001	12	2.546 ± .002	2.546 ± .001
500	14	3.799 ± .008	6	3.796 ± .003	3.799 ± .002
800	6	5.363 ± .005	6	5.367 ± .003	5.365 ± .003
1000	7	6 257 ± .008	7	6.255 ± .005	6.256 ± .004

[a] Some additional runs were made at 25° which introduced slight changes in some of the values previously published.

amounts to only about 0.1% so that even a 50% error would not change the absorption coefficient by more than 0.05%. The change of vapor pressure with total pressure on the liquid is given by the Poynting relationship[7]

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(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 183.

$$\left(\frac{dp}{dP}\right)_T = \frac{\bar{V}}{v}$$

In this case p and P are the vapor pressure of water and the total pressure on the liquid, respectively, while $\bar{V}$ is the partial molal volume of water vapor and v that of water. Since the partial molal volumes are not known, the molal volumes were taken in each case. For the 100° isotherm the Callendar equation was assumed to represent the behavior of water vapor while for all others the perfect gas law was used. For the 100° isotherm the Poynting equation took the following form

$$A \ln \frac{P}{P_0} - B(p - p_0) = V_0(P - P_0) - aP^2 + bP^3 - cP^4 \; ^{8}$$

The data for the compressibility of water at 100° were taken from an extrapolation of the data of Bridgman.[9]

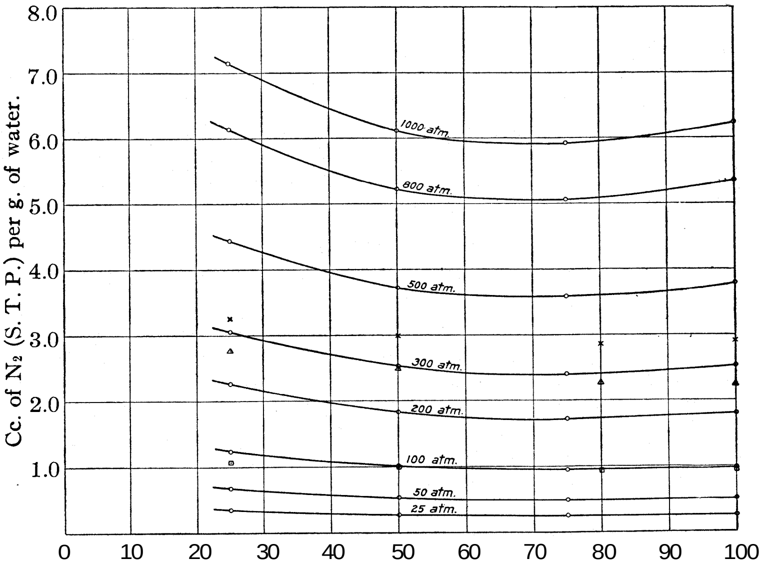

Fig. 2.— 8, Goodman and Krase at 100°; △, **Goodman and Krase at** 200°; X, **Goodman and Krase at** 300°.

The more recent data of Tammann[10] show a slightly different trend. The change of vapor pressure with total pressure has been discussed by Bartlett,[11] Lurie and Gillespie[12] and others. Bartlett measured the concentration of water vapor in compressed nitrogen and hydrogen in the presence of the condensed phase.

(8) Dr. W. Edwards Deming suggested a convenient graphical method of solving this equation

(9) Bridgman, "International Critical Tables," Vol. III, p. 40.

(10) Tammann and Ruhrenbeck, Ann. *phys.*, 13, 63 (1932)

(11) Bartlett, THIS JOURNAL, 49, 65 (1927)

(12) Lurie and Gillespie, *ibid.*, 49, 1146 (1927).

Isobars are plotted in Fig. 2. The data show a minimum at about 70° which becomes more pronounced as the pressure rises. The question of the actual existence of minima of solubility of gases in water has until quite recently been a controversial matter. Bohr and Bock[13] first found a minimum in the case of hydrogen, but their work was thought to have systematic errors.[14] Recently Ipatiew and co-workers[15] mention the possibility of a minimum for hydrogen between 65 and 75°. The minimum for helium that was thought to have been discovered by Estreicher[16] at about 25° has been discredited by Cady and associates[17] and more recently by Lannung.[18] Goodman and Krase[1] found a minimum for nitrogen but its location is not in very good agreement with the one in this work, as will be seen from Fig. 2. A comparison with the work of Frolich and associates was made previously.[3] Kuenen,[19] reasoning from the known behavior of mixtures, suggested that every gas should show a minimum of solubility and that for sparingly soluble gases this minimum should occur at low temperatures. The solubility of nitrogen in many organic substances increases with rise in temperature over the known range.[20] Figure 3 shows

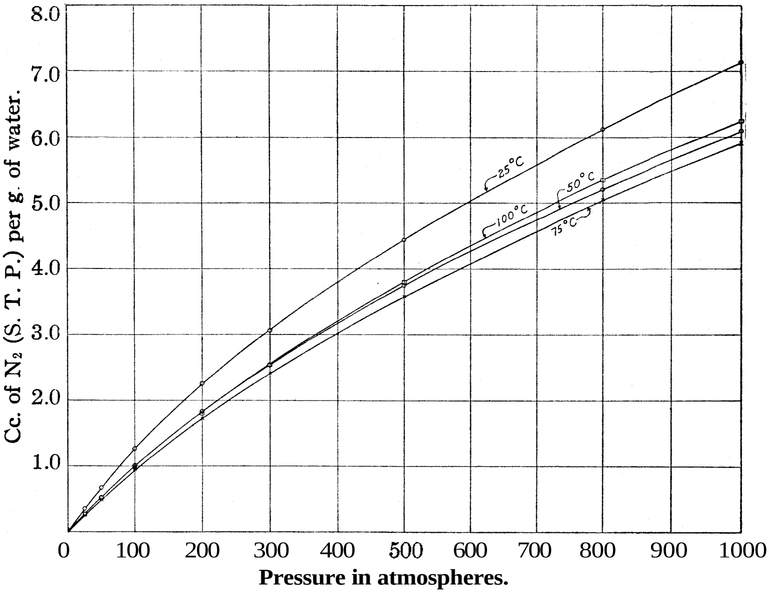

Fig. 3.

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(13) Bohr and Bock, *Wied. Ann.*. 44, 318 (1891).

(14) Drucker and Moles, *Z. physik. Chem.*, **75**, 405 (1911).

(15) Ipatiew, Drushina Artemowitsch and Tichomirow, *Ber.*, 65, 568 (1932).

(16) Estreicher, *Z. physik. Chem.*, *31*, 176 (1899).

(17) Cady, Elsey and Berger, THIS JOURNAL, 44, 1456 (1922).

(18) Lannung, *ibid.*, **52**, 68 (1930).

(19) Kuenen, *Proc. Roy. Soc. Edinburgh*, **23**, 312 (1900); Kuenen, "Verdampfung und Verflüssigung von Gemischen," Johann Ambrosius Barth, Leipzig, 1906, p 82.

(20) Just, *Z. physik. Chem.*, **37**, 342 (1901).

more clearly the fact that at higher pressures the solubility of nitrogen at 100° is already greater than at 50°.

Figure 4 finally indicates the impossibility of predicting the solubility of gases at high pressures from any simple considerations. Henry's law

$$p = kc$$

where p is the partial pressure of the gas and c the concentration in the liquid does not hold as shown in Fig. 4. Substitution of fugacity for pressure actually makes the agreement worse at higher pressures. The dotted curve in Fig. 4 was calculated from the Ostwald absorption coefficient.

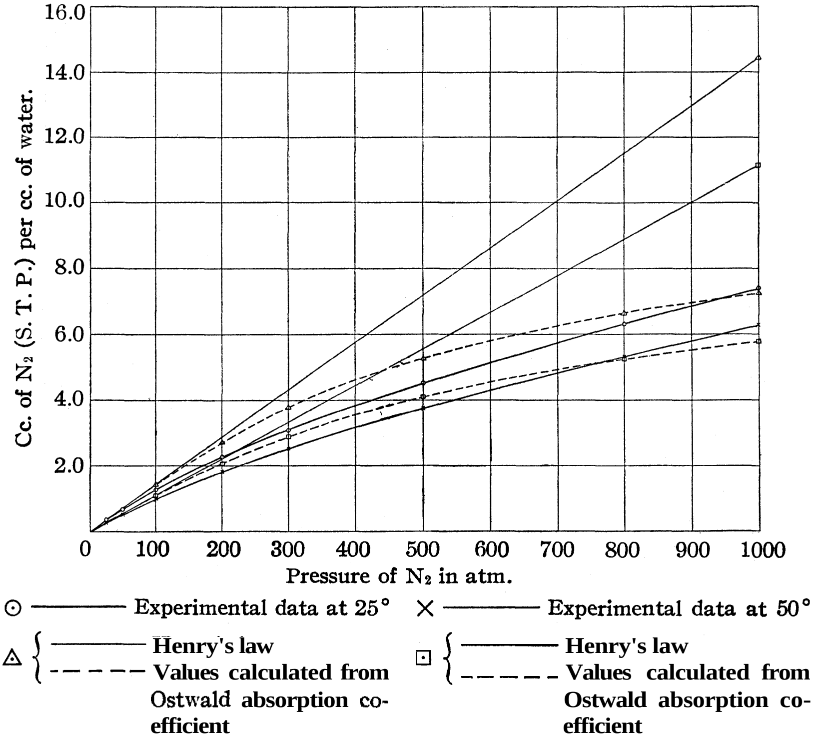

Fig. 4.

$$\lambda = \frac{\text{concn. in gas phase, g./cc.}}{\text{concn. in liq. phase, g./cc.}}$$

λ being obtained from the solubility at one atmosphere partial pressure.[21] The volume of water was corrected for compressibility, neglecting the solubility effect. The values calculated from the absorption coefficient are in much better agreement. The curves for 75 and 100° are not shown, but are of somewhat similar nature.

(21) For calculation of the fugacities and densities of nitrogen, see Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931).

Summary

A simple apparatus and method for obtaining solubilities of gases in water and similar liquids has been described.

The solubilities of nitrogen in water at 50, 75 and 100° from 25 to 1000 atmospheres were measured.

The absorption coefficient showed a distinct minimum at about 70° which became more pronounced with increase in pressure.

It has been shown that at present it is not possible to predict the solubility of nitrogen in water at high pressures from low pressure data with any degree of certainty

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY, UNNERSITY OF DENVER]

Luminescence and Crystalline Structure[1]

BY BYRON E. COHN

Many inorganic solids exhibit luminescence which may appear as fluorescence, phosphorescence or thermoluminescence. Small quantities of dissolved inorganic materials may confer upon these solids the ability to gather energy which may be emitted as luminescence. Such dissolved substances are termed activators. Lenard[2] has proposed the hypothesis that the absorbing and re-emitting center in luminescent solids consists of an atom or molecule of the activator linked with a definite number of solvent molecules. This investigator attributed each luminescence band to a different type of center. In recent years the hypothesis of Lenard has been transposed into a modified form in which it is stated that the manner of linkage of an atom of the activator with a definite number of solvent atoms occurs by substitution of the activator atom for one of the solvent atoms in a definite crystalline lattice.

Tiede and his co-workers[3] have presented some experimental evidence for the crystalline structure theory of luminescence. These workers find that the property of luminescence appears coincident with the occurrence of marked crystalline structure both in the case of calcium tungstate and boron nitride phosphors. On the other hand, Lenard and his students[4] stated that the Lenard phosphors (alkaline earth sulfides oxides or selenides) appear to be hardened glass-like materials. In view of the contradictory statements and'the somewhat indirect evidence, information

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(1) Presented in part before the Physical and Inorganic Division at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

(2) Lenard, *Sitz. Heidelb.* Akad., 1917, 1918.

(3) Tiede and Schleede, *Z. Elektrochem.*, 89, 305 (1923); Tiede and Tornaschek, *ibid.*, 29, 303 (1923); Schleede, Z. *Physik*, 18, 109 (1923).

(4) Pringsheim, "Fluorescenz und Phosphorescenz," Julius Springer, Berlin, 1928, p. 263.

which will furnish a more definite answer to the question should be of value.

The Relation of the Optimum Concentration to Crystalline Structure.—It has been found by numerous workers in the past that whenever an activator is responsible for luminescence there is found a certain concentration of activator at which the luminescence is of greatest intensity. This concentration is termed the optimum concentration. The optimum concentration is related to the number of atoms which constitute a single lattice group in the crystal theory of luminescence. Late in 1930 Ewles[5] developed a mathematical relation between concentration and intensity of luminescence based upon the substituted activator atom crystal lattice theory. He found that to a first degree of approximation the intensity for a single luminescence band would be given by the expression

$$F = ACe^{-nC}$$

where F is the intensity, A a constant, C the concentration of activator, and n the number of solvent atoms in one crystal group. Ewles pointed out that differentiation of this function indicates that the maximum value of the intensity will be found at the concentration $C = 1/n$. Therefore, the determination of the optimum concentration gives the value of n, the number of solvent atoms associated with each activator atom in the crystal lattice. Without recourse to any formal mathematics it seems evident that if the luminescence is to be conditioned only by the assumption that an atom of activator is linked with a definite number of solvent atoms, the optimum concentration will be the one at which this particular ratio exists. Conversely, if at the optimum concentration the ratio of the number of activator atoms to solvent atoms is $1/S$ then the inference may be drawn that one activator atom would be associated with S solvent atoms in each Lenard center. Moreover, this would be true whether or not the group was a crystalline unit.

Nyswander and Cohn[6] have observed that zinc borate glasses which contain manganese as an activator exhibit thermoluminescence when exposed to ultraviolet light. The relation of the intensity of luminescence to the concentration of manganese has been measured accurately by Cohn and Harkins.[7] The optimum concentration of manganese in the case of thermoluminescence is close to 0.2% manganese. The optimum concentration is not changed when the exciting light is passed through a Corex A blue-purple filter (thickness 4.26 mm.), although the intensity of thermoluminescence is markedly reduced. This indicates that the optimum concentration for thermoluminescence does not vary with the wave length of exciting light in the region examined.

It has been found that zinc borate glasses which contain manganese ex-

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(5) Ewles, *Proc. Roy. Soc.* (London), *129*, **509** (1930).

(6) Nyswander and Cohn, *J. Optical Soc. Am. 20*, **131** (1930).

(7) Cohn and Harkins, THIS JOURNAL, **52**, 5146 (1930).

hibit fluorescence' when exposed to ultraviolet light. The relation of fluorescence intensity to concentration of manganese is represented by the curves of Fig. 1. Curve A represents the relative intensities of fluorescence obtained when the exciting ultraviolet light passed through a Corex A blue-purple filter of thickness 4.26 mm. whose transmission limit was about 2350 Å. Curve B represents the relative values of fluorescence when the exciting ultraviolet light was transmitted through a Corex A red-purple filter of thickness 4.22 mm. whose transmission limit was about 2480 Å. It will be noted that the optimum concentration is approximately 1.75% manganese in both cases, although the efficiency of excitation of fluorescence is greater for the shorter wave lengths. This signifies that the optimum concentration for fluorescence is independent of the wave length of exciting light in the region of the spectrum in which thermoluminescence may also be excited.

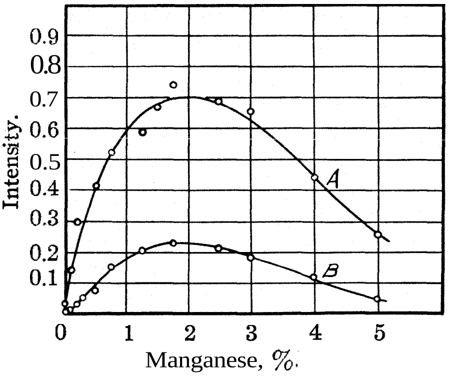

Fig. 1.—The intensity of fluorescence of zinc borate glasses which contain manganese. Curve A represents intensities when excited through a filter of transmission limit 2350 Å.; Curve B, 2480 Å.

The values of the intensity of fluorescence were obtained with the aid of a fluorescence camera whose construction is indicated in Fig. 2. A represents a quartz mercury arc, V a Corex A filter which passed the exciting ultraviolet light, but not the visible of wave length longer than about 4500 Å. S is the glass sample which is 6 mm. square and 2.6 mm. thick, with polished faces and ground upon the edges with emery flour. F indicates a second filter which transmitted red light of wave lengths greater than 5900 Å. L is the lens which passed the fluorescent light from the sample S to the photographic plate. The latter is carried by a rack and pinion upon the back of the camera B. The exciting light passed through the filter to the sample S and a fluorescent comparison sample S' in the same plane as S but not shown in the diagram. The fluorescent light emerged from the edge of the sample S and the comparison sample S' and was photographed. By this means a photographic record of intensities of a series of samples

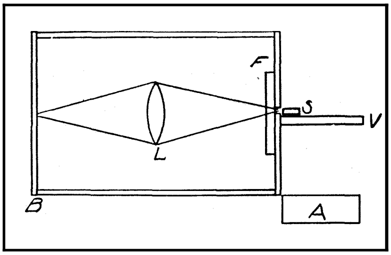

Fig. 2.—Simplified section through fluorescence camera: A, quartz mercury arc; V, filter for ultraviolet light; S, glass specimen; F, filter transparent to fluorescent light; L, lens.

each having the intensity of the comparison alongside was obtained upon a single photographic plate. The density of the deposit upon the photographic plate was determined with the aid of a photoelectric densitometer. The latter consisted of a lamp operated at constant voltage with the aid of a Delta regulating transformer; a small half circle opening over which the images of the plate could be placed; a Weston photronic cell; and a galvanometer. The fluorescent intensities represented in Fig. 1 were graphed in terms of the density of the photographic image obtained after a three-minute exposure to the fluorescence excited by a mercury arc in fused quartz ("Lab-Arc") operating upon 2 amperes, alternating current.

In Fig. 3 Curve A represents the intensity of thermoluminescence and Curve B, the intensity of fluorescence as affected by the concentration of the manganese which served as the activator. The intensity coordinates are not equal for the two curves. Inasmuch as the zinc borate glass solvent which composed the specimens had a composition equivalent to $Zn(BO_2)_2 \cdot {}^1/_4 ZnO$, the ratio of the number of zinc atoms to manganese atoms in each of the lattices suggested by the data from the optimum was readily computed. In thermoluminescence the ratio of zinc to manganese atoms in a lattice group would be 200 to 1, whereas in the case of fluorescence the ratio of zinc to manganese atoms would be 23 to 1. Each sample of zinc borate glass which contained manganese exhibited both fluorescence and thermoluminescence and therefore would contain both lattice groups. At this stage of presentation of experimental evidence, therefore, two different crystalline lattices would be indicated as being present in each specimen on the basis of the crystal lattice theory.

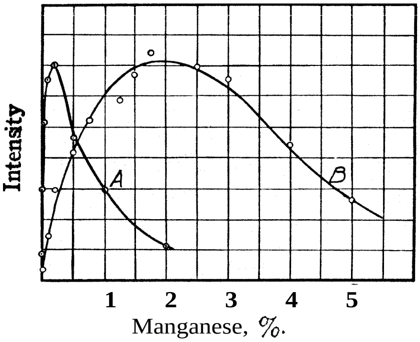

Fig. 3.—Curve A, intensity of thermoluminescence of zinc borate glasses which contain manganese; Curve B, intensity of fluorescence of similar glasses.

The Relation of the Emission Spectrum to Crystalline Structure.—If the luminescence of an inorganic solid is to be attributed to a unit lattice grouping, the spectrum of the luminescence is also to be assigned to this unit. This is postulated by both the Lenard and the crystal lattice theories. It is therefore pertinent to our problem to investigate the comparative spectra of fluorescence and thermoluminescence.

The emission spectrum of fluorescence was secured. This spectrum is a band extending from about 5670 to 6750 Å. The maximum intensity is about 6100 Å. The photographic exposure was made upon a panchromatic plate. The exposure time was two hours. An "extreme red" sensitive plate showed no detectable darkening in the region 7200 to 7600 Å. after a ten-hour exposure, which indicates that the panchromatic plate is sensitive in the spectral region occupied by the fluorescence band. The experimental arrangement was similar to that which is used to obtain Raman spectra. The emission spectrum of thermoluminescence was next obtained. Efforts to accomplish this were unsuccessful until an improvised spectrograph of large light gathering power was constructed in which the thermoluminescence sample served as its own slit. The thermoluminescence emission spectrum, photographed upon a panchromatic plate, was found to be a band in the same region of the spectrum as that of fluorescence. The maximum intensity was 6050 +50 Å.

The evidence indicates that the emission spectra of fluorescence and thermoluminescence are alike, within experimental error. The luminescence therefore should be occasioned by a single lattice group. The conclusion given by evidence from the condition of the optimum was that two crystalline groups were present in each specimen of the zinc borate glass which contained manganese. The conclusion presented by the evidence from emission spectra is in direct conflict with that obtained from the conditions of the optimum as based upon the substituted crystal lattice theory. Therefore, the results indicate that the crystalline structure theory does not account for the luminescence of zinc borate glasses which contain manganese as the activator.

In order to correlate this evidence with x-ray crystal analysis data, powder photographs of zinc borate glasses which contained manganese were taken. The specimens were exposed for the long period of two hundred and forty hours in a Hull powder x-ray diffraction apparatus. The resulting films presented no lines which would indicate the occurrence of crystal planes.

Summary

1. Zinc borate glasses which contain manganese have been found to exhibit fluorescence when exposed to ultraviolet light.

2. The relation of intensity of fluorescence to concentration of manganese has been determined.

3. The emission spectrum of fluorescence has been obtained and is a band extending from about 5670 to 6750 Å. with its maximum in the region of 6100 Å.

4. The thermoluminescence emission spectrum has been obtained and has been found to be a band with a maximum at 6050 + 50 Å.

5. Results obtained have been interpreted in the light of the substituted crystalline lattice theory. It is concluded from these results that this theory does not account for luminescence in zinc borate glasses.

DENVER, COLORADO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Effect of Ethylene Glycol upon the Activity of Sulfuric Acid in Aqueous Solutions

BY H. M. TRIMBLE AND P. F. EBERT

Numerous studies have been made of the activities of electrolytes in aqueous solutions. A few studies have also been made of the effect upon activity produced by adding to the solutions such solvents as ethyl alcohol,[1] methyl alcohol[2] and glycerol.[3] Such studies have importance in connection with the theory of solution, and they should aid also in gaining an understanding of the kinetics of reactions in mixed solvents. For example, it has recently been found[4] that the inversion of sucrose in the presence of sulfuric and hydrochloric acids as catalysts is promoted at some concentrations of glycol and retarded at others. Such behavior calls for further study. This paper presents the results of a study, by electrometric methods, of the activity of sulfuric acid in aqueous solutions in the presence of ethylene glycol.

Reagents.—Ethylene glycol was prepared for these experiments by the method which has been described previously.[5] The water which was used in making up the solutions was redistilled from alkaline permanganate solution in a still constructed throughout of Pyrex glass. C. P. sulfuric acid was used in making up stock solutions, whose acid content was then determined by precipitating the sulfate ion as barium sulfate and weighing as such. The hydrogen was a commercial electrolytic product. A small quantity of oxygen was removed from it by passing it over a glowing platinum wire. It was then passed through a washing bottle filled with water, next through a washing bottle immersed in the bath and filled with the liquid which was to be studied, and then to the hydrogen electrode vessel. Mercury was purified by distillation by the method of Hulett.[6] Mercurous sulfate was prepared by the method of Wolff and Waters.[7] Two samples from different preparations and a special "analyzed" commercial material were used to make up a number of mercurous sulfate electrodes, each with molar sulfuric acid as the electrolyte, and these electrodes were carefully compared. They were found to give the same potentials to one or two hundredths millivolt. Since the commercial material was satisfactory and more readily available it was used in nearly all of the experiments.

In preparing the solutions the desired quantities of stock sulfuric acid solution and of glycol were weighed out and washed into a calibrated volumetric flask, the flask was then filled very nearly to the mark, agitating to ensure thorough mixing, and brought to 25° in the thermostat. The meniscus was then brought exactly to the mark by adding water, also at 25°, and the solution was again thoroughly mixed.

Apparatus and Procedure.—The measurements were made using a calibrated po-

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(1) Among others: Harned and Fleysher, THIS JOURNAL, 47, 92–95 (1925); Scatchard, *ibid.*, 47, 2098–2111 (1925); 49, 217–218 (1927); Bronsted and Williams, *ibid.*, 50, 1338–1343 (1928).

(2) Åkerlöf, *ibid.*, 52, 2353–2368 (1930).

(3) Lucasse, *ibid.*, 48, 626–631 (1926).

(4) Young and Trimble, *J. Phys. Chem.*, 36, 830–841 (1932).

(5) Trimble, *Ind. Eng. Chem.*, 23, 165 (1931).

(6) Hulett, *Phys. Rev.*, 32, 257 (1911).

(7) Wolff and Waters, Sci. Paper 70, U. S. Bureau of Standards, (1907).

tentiometer. A standard Weston cell of the unsaturated type, whose potential was certified by the manufacturers, was used as reference standard. Measurements were carried out in a thermostat filled with gas oil, and maintained at 25 ± 0.02°.

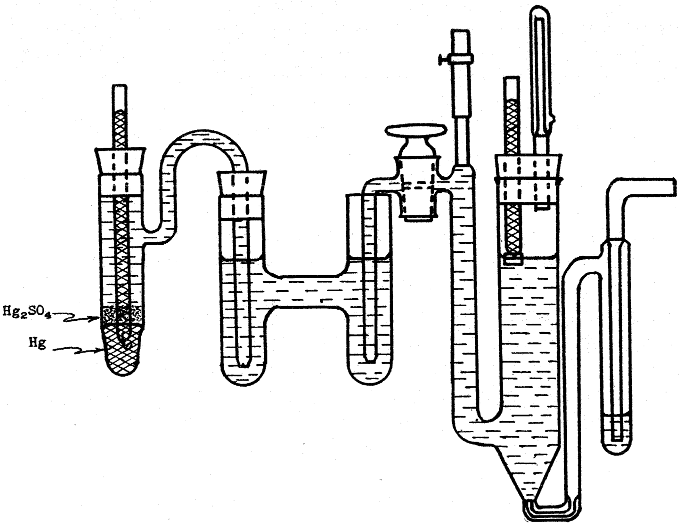

Fig. 1.—Cell assembly.

A diagram of the complete cell as assembled is shown in Fig. 1; the device used for filling the mercurous sulfate half cell is shown in Fig. 2. Mercurous sulfate was first washed thoroughly with the solution to be used, and then the solution was saturated with it by rotating the two together for about twelve hours. The rubber stopper placed on the side tube of the electrode vessel was coated with Lubriseal to ensure an air-tight connection. Mercury was introduced into the vessel, the stopper bearing the tube with

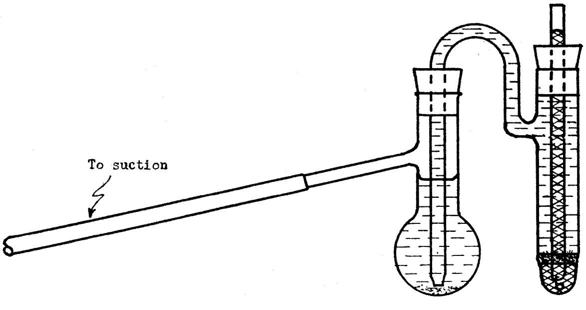

Fig. 2.—Device for filling mercurous sulfate electrodes.

its platinum wire through which contact with the mercury was established was coated with Lubriseal and inserted, the small distilling flask was filled with the solution containing a suspension of mercurous sulfate, and then connected to the electrode vessel. Upon evacuation the solution was readily freed of its gases, and on releasing the suction the mercurous sulfate half cell was completely filled. Such electrodes were found to be practically at equilibrium at the start, and maintained constant and reproducible potentials, with a given solution, indefinitely. The hydrogen electrode vessel was a modified form of the Walpole vessel. The gas outlet tube prevented back pressure by allowing the gas to escape upward through a very narrow annular space. The vessel was filled with the same solution as was the mercurous sulfate half cell, but, of course, containing no mercurous sulfate. An H tube filled with the same solution served to connect the two half cells.

After filling and assembling, the cell was placed in the bath and the liquid in the hydrogen half cell was thoroughly saturated with hydrogen, the cell being lightly stoppered. The platinum electrode was, meanwhile, saturated with hydrogen by making it the cathode in a dilute solution of sulfuric acid, passing only a small current. When ready to start, the electrode was quickly washed with conductivity water, then several times with more of the solution which had been put into the cell, and then it was brought into its place. Readings were started at once and continued for four to six hours. The potential generally became constant in twenty to thirty minutes. No results were accepted from experiments in which the potential failed to remain constant thence throughout the time of observation.

No variation in potential was at any time detected such as would indicate that glycol was combining with the acid. Special experiments were performed by one of us tc determine whether glycol can combine either with sulfuric acid or hydrochloric acid. No reaction was ever found, since the titratable acidity remained constant for as long as five weeks. Acetic acid, on the other hand, showed a regular decrease in titratable acidity. The solutions contained as high as 3 moles of acid and 5 moles of glycol per liter. Glycol does not seem to poison platinized platinum electrodes; and the potentials are, if anything, more constant and reproducible in the presence of glycol than in its absence.

Experimental Results

The potentials as measured are set forth in Table I. Each value represents the mean of at least three very concordant determinations.

TABLE I

E. M. F. VALUES FOR THE CELL H_2^-, H_2SO_4 (GLYCOL), Hg_2SO_4, Hg^+

Mole H_2SO_4 per liter	Mole glycol per liter 0	1	5	10
0.005	0.8162	0.8130	0.7994	0.7834
.025	.7738	.7705	.7592	.7453
.050	.7546	.7529	.7422	.7290
.25	.7152	.7108	.7018	.6904
.50	.6952	.6933	.6844	.6730
1.00	.6744	.6730	.6633	.6505

TABLE II

DENSITIES OF H_2SO_4–GLYCOL–H_2O SOLUTIONS

Mole H_2SO_4 per liter	Moles of glycol per liter 0	1	2.6	5	10
0.0	0.9971	1.0049	1.0164	1.0364	1.0720
.005	.9975	1.0052	1.0167	1.0367	1.0723
.025	1.0001	1.0065	1.0179	1.0379	1.0735
.050	1.0008	1.0080	1.0194	1.0393	1.0748
.10	1.0038	1.0114	1.0229	1.0424	1.0774
.25	1.0131	1.0207	1.0319	1.0511	1.0858
.50	1.0285	1.0358	1.0470	1.0655	1.0995
1.00	1.0589	1.0660	1.0765	1.0943	1.1269

To evaluate the data properly it was essential to have, also, the densities of these solutions. These were determined at 25°, using Sprengel type pycnometers, with the results as set forth in Table II. Values for solutions containing 0.005, 0.025 and 0.050 mole of sulfuric acid per liter were secured by interpolation. Other values are as measured.

Method of Calculating Activities

The orthodox method for calculating the activities of electrolytes in solution from e. m. f. data using such cells as ours has been given by Lewis and Randall.[8] It involves the use of the equation, for sulfuric acid

$$0.08873 \log_{10} \frac{a_{\pm}}{m} = 0.08873 \log_{10} \gamma = E^0 - (E + 0.08873 \log_{10} m)$$

where a, is the geometric mean activity of the ions, γ is the activity coefficient, E is the electromotive force of the cell and E^0 is the value which is approached by the quantity in parentheses above, which is called $E^{0'}$, as the acid approaches infinite dilution in concentration. For our work it is necessary to take m as the number of moles of sulfuric acid in 1000 g. of solvent, whether this solvent be pure water or a mixture of water and glycol. This, in itself, is not particularly open to objection. It is the convention which is often adopted in connection with the equations of the Debye–Hückel theory.[9] Even with this convention, however, the handling of the data is difficult. Extrapolations to infinite dilution cannot be made with certainty because the electromotive forces of cells using very dilute solutions cannot be determined with sufficient accuracy. It happens that, in dilute solutions, in many cases the potentials of cells such as are here used are rectilinear functions of the logarithms of the mole fractions of the electrolytes in the solution. For sulfuric acid solutions, as will be shown, this is true up to concentrations of about 0.85 mole per liter. This permits the use of the equation, closely analogous to that of Lewis and Randall

$$0.08873 \log_{10} \frac{a_{\pm}}{N} = E_N - (E + 0.08873 \log_{10} N) \qquad (1)$$

where N is the mole fraction of sulfuric acid in the solution, and E_N is the limiting value of the quantity in parentheses, here called E'_N, which is found when the graph of E'_N against $\log_{10} N$ is extrapolated to zero. It must be emphasized that this equation describes the relations between the quantities represented for those solutions in which E is a rectilinear function of log N. If this relation were to persist up to the point where pure sulfuric acid is reached, then we might reasonably take a, $= N = 1$. E_N, then, would be the voltage of a cell such as ours, containing pure sulfuric acid. The graph of E'_N against log N up to a definite limit, as will be shown, is a straight line, which makes the extrapolated value, E_N very easy to arrive at and very certain.

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(8) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, pp. 332–335.

(9) Lucasse, Ref. 3, p. 627.

To illustrate and justify the application of this equation, we have employed the data for the cell (Hz, H_2SO_4 (m), Hg_2SO_4, Hg) as given in "International Critical Tables."[10] Table III will be self-explanatory. Values of N, the mole fraction, are readily found from the molalities of the solutions, using the equation

$$N = \frac{m}{m + 55.51}$$

TABLE III

DATA FOR CALCULATION OF E_N FOR CELLS

m H_2SO_4	N	E	E'_N	m H_2SO_4	N	E	E'_N
0.005	0.000090	0.8160	0.4570	0.8453	0.0150	0.6812	0.5193
.05	.00090	.7546	.4843	1.133	.0200	.6720	.5212
.1112	.00198	.7343	.4944	2.922	.0500	.6315	.5160
.2789	.0050	.7114	.5073	4.827	.0800	.5915	.5002
.5607	.0100	.6929	.5154				

Values of E'_N are plotted against log N in curve I of Fig. 3. The points from this table are indicated by means of circles. The data are adequately represented by the equation

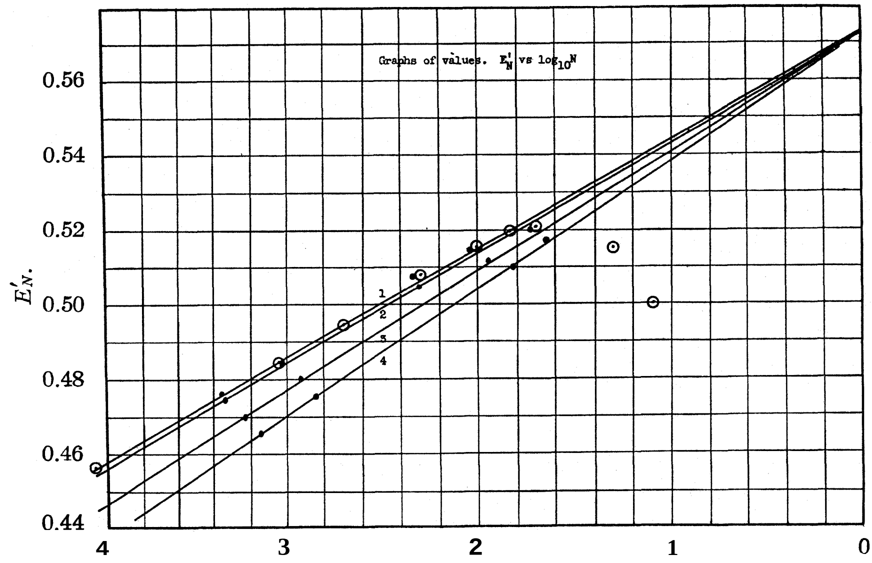

Fig. 3.—Graphs of values of E'_N vs. $\log_{10}$ N.

$$E'_N = 0.5724 + 0.0287 \log_{10} N \qquad (2)$$

whence it follows that $E'_N = 0.5724$. Obviously equation (2) ceases to hold for solutions in which $\log_{10}$ N is less than -1.825. This corresponds to a concentration of approximately 0.85 molal. Since, by definition,

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(10) "International Critical Tables," Vol. VI, p. 323.

$E'_N = E + 0.08873 \log_{10} N$, we may substitute in this equation the equivalent of E'_N from equation (2), and get

$$E = 0.5724 - 0.0600 \log_{10} N \tag{3}$$

Using equation (3) and the proper values for N we have calculated E for the cells involved. Column 2 of Table IV gives these values; and, for comparison, column 3 gives the values of E from "International Critical Tables." Perhaps the best test of the essential correctness of the method lies in the fact that, as shown here, the potentials of galvanic cells using the various solutions of sulfuric acid can be calculated by means of equation (3) with an average error of ± 0.00065 volt, an accuracy which is of the same order of magnitude as the accuracy of the potentials given, which is, according to "International Critical Tables," about ± 0.0002 volt. The potential calculated for 1.133 molal sulfuric acid has been omitted from this analysis of errors, as it lies outside the range within which these equations hold accurately. The errors of prediction, moreover, are consistent, since three potentials as calculated are slightly too high and three are slightly too low, and the average positive and negative errors are very nearly the same.

Substituting (2) in (1), we may write

$$\begin{aligned} 0.08873 \log k'a_{\pm} &= E_N - E'_N + 0.08873 \log_{10} N \qquad (4) \\ &= (-0.0287 + 0.0887) \log_{10} N = 0.0600 \log_{10} N \end{aligned}$$

and

$$\log_{10} k'\, a, = \frac{0.0600}{0.08873} \log_{10} N = 0.6766 \log_{10} N \tag{5}$$

Using equation (5) we have calculated values of activity for these same solutions. They may be found in column 4 of Table IV. The activities of sulfuric acid in its solutions, as calculated from the data of Lewis and Randall[11] are given in column 6. The γ values given by Lewis and Randall were plotted against the corresponding molalities. From the curve drawn through the points, values of γ corresponding to the molalities of Table IV were read off and multiplied by the molalities to get a, From the comparative values it is obvious, however, that equation (5) gives, not activi-

TABLE IV

CHECK UPON THE METHOD OF CALCULATION

Values of E and of a,, calculated

m H_2SO_4	E calcd.	E found	$k'\, a_{\pm c}$	$a_\pm$ calcd.	$a_\pm$ from L. and R.
0.005	0.8153	0.8160	0.00183	0.0041	0.0035
.05	.7553	,7546	.00869	.0194	.0199
.1112	.7345	.7343	.01481	.0332	.0334
.2789	.7105	.7114	.02779	.0622	.0600
.5607	.6925	.6929	.04434	.0993	.0953
.8453	.6820	.6812	.05828	.1305	.1345
1.133	.6744	.6720	.07088	.1588	.1700

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[11] Lewis and Randall, Ref. 8, pp. 344 and 357.

ties, but simply quantities proportional to them, namely, values of $k' a$, On the average $k' a$, multiplied by the factor 2.240 gives values of activity. These are given in column 5 of the table.

The agreement between these values of a, and those calculated by means of equation (5) is fairly good. So far as the authors are aware, this method of calculating the activities of electrolytes in dilute solutions from electromotive force data has not previously been employed.

This method of calculating activities has been applied to the data of our experiments. The essential data for the drawing of the curves and values of E calcd. are given in Table V. In this table N was calculated from the densities of the solutions and the weights of glycol and sulfuric acid known to be present.

TABLE V

H_2SO_4–H_2O (GLYCOL) SOLUTIONS, ESSENTIAL DATA FOR CURVES

Part 1. No glycol					Part 3. 5 Moles of glycol per liter				
Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.	Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.
0 005	0.00009	0.4572	0.8162	0.8153	0.005	0.00011	0.4481	0.7994	0.7992
025	.00045	.4768	.7738	.7731	.025	.00055	.4700	.7592	.7592
050	.00090	.4843	.7546	.7549	.050	.00110	.4796	.7422	.7419
.25	.0045	.5070	.7152	.7133	.25	.00550	.5013	.7018	.7019
50	.0091	.5141	.6952	.6949	.50	.01118	.5112	.6844	.6842
85	.0156			.6808	.85	.0192			.6708
1 00	.0184	.5205	.6744	.6766	1.00	.0227	.5174	.6633	.6666
Part 2. 1 Mole of glycol per liter					Part 4. 10 Moles of glycol per liter				
0005	0.000094	0.4557	0.8130	0.8121	0.005	0.000143	0.4422	0.7834	0.7835
.025	.00047	.4752	.7705	.7705	.025	.000714	.4660	.7453	.7452
050	.00094	.4843	.7529	.7526	.050	.00143	.4766	.7290	.7286
.25	.00471	.5043	.7108	.7110	.25	.00714	.4998	.6904	.6903
.50	.00946	.5137	.6933	.6929	.50	.0145	.5098	.6730	.6733
.85	.0162			.6790	.85	.0251			.6603
1.00	.0191	.5205	.6730	.6747	1.00	.0297	.5150	.6505	.6562

On plotting the values of E'_N against $\log_{10}$ N in each case the following equations, analogous to equation (3), are found to represent the data very satisfactorily

$$E'_N = 0.5724 + 0.0287 \log_{10} N \qquad (2)_0$$

$$E'_N = 0.5724 + 0.0292 \log_{10} N \qquad (2)_1$$

$$E'_N = 0.5724 + 0.0314 \log_{10} N \qquad (2)_5$$

$$E'_N = 0.5724 + 0.0338 \log_{10} N \qquad (2)_{10}$$

The subscripts of the equation numbers in each case refer to the number of moles of glycol present per liter of solution. The curves are numbers 2, 3 and 4 of Fig. 3. The curve for solutions containing no glycol falls upon that found from the data from "International Critical Tables," discussed above. Since the constant term of the linear equation comes out the same in each case, it is unnecessary in this method of calculation to derive a relation between limiting values of E'_N for different concentrations of glycol in order to be able to calculate activities in solutions containing glycol in relation to those which contain no glycol.[12] The activities, then, are functions only of the mole fraction of the sulfuric acid and the concentration of glycol in the solution. Proceeding just as before (equation 3) it may be shown that the following equations hold for the voltages of the cells at different concentrations of glycol.

$$E = 0.5724 - 0.0600 \log_{10} N \qquad (3)_0$$
$$E = 0.5724 - 0.0595 \log_{10} N \qquad (3)_1$$
$$E = 0.5724 - 0.0573 \log_{10} N \qquad (3)_5$$
$$E = 0.5724 - 0.0549 \log_{10} N \qquad (3)_{10}$$

A comparison of the values of "E calculated" with those found, as set forth in Table V, shows the validity of our method of calculation. It appears, again, that the range over which it holds does not quite extend to one mole of sulfuric acid per liter. It seems reasonable, in view of the agreement shown in Table IV, to assume that it holds, within the limits of experimental error, to concentrations as great as 0.85 mole per liter. Experiments just completed give for 5 moles of glycol and 0.85 mole of sulfuric acid per liter, a voltage of 0.6707, in excellent agreement with the calculated value which is 0.6708. Partial data for this concentration of sulfuric acid have, therefore, been inserted in Table V.

Proceeding as in the derivation of equation (5) we have for calculation of values of $k'a,$

$$\log_{10} k'a, = 0.6766 \log_{10} N \qquad (5)_0$$
$$\log_{10} k'a, = 0.6706 \log_{10} N \qquad (5)_1$$
$$\log_{10} k'a, = 0.6461 \log_{10} N \qquad (5)_5$$
$$\log_{10} k'a, = 0.6191 \log_{10} N \qquad (5)_{10}$$

$k'a,$ is here used, since, as has been shown, the calculated value is only proportional to, not equal to $a,$. This latter value is found in each case by multiplying $k'a,$ by the factor 2.240. The values of $a,$ as calculated are shown in column 3 of Table VI.

The equations developed above by means of which E and $k'a,$ may be calculated from our data involve, in the coefficients of the variable terms, the slope of the straight line which is obtained when E'_N is plotted against $\log_{10} N$ for each number of moles of glycol per liter. This slope is a rectilinear function of the number of moles of glycol per liter in the solutions. The relation is $k = 0.0287 + 0.00052$ G where k is the multiplying factor in the equation $E'_N = 0.5724 + k \log_{10} N$ for any given number of moles of glycol per liter, and G is the number of moles of glycol. We may now write the following general equations, which give E and $k'a,$ in terms of moles of glycol per liter and mole fraction of sulfuric acid for any such solutions as these

$$E = 0.5724 - [0.0887 - (0.0287 + 0.00052\,G)] \log_{10} N \qquad (6)$$
$$= 0.5724 - [0.0600 - 0.00052\,G] \log_{10} N \qquad \text{general}$$

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[12] See Scatchard, THIS JOURNAL, 47, 2105 (1925).

and

$$\log k' a_{\pm} = \left[\frac{0.0600 + 0.00052\,G}{0.08873}\right] \log_{10} N \qquad \begin{matrix}(5)\\ \text{general}\end{matrix}$$

TABLE VI

H_2SO_4–H_2O–GLYCOL SOLUTIONS. VALUES OF m, $a_{\pm}$ FOR H_2SO_4 AND F OF THE REACTION

Part 1. No glycol					Part 3. 5 Moles of glycol per liter				
Mole H_2SO_4 per liter	m	$a_{\pm}$	ΔF reaction	γ	Mole H_2SO_4 per liter	m	$a_{\pm}$	AF reaction	γ
0.005	0.005	0.0041	−37,625	0.820	0.005	0.005	0.0062	−36,882	1.240
.025	.025	.0122	−35,678	.488	.025	.025	.0175	−35,037	0.700
.050	.050	.0195	−34,838	.390	.050	.049	.0274	−34,238	.559
.25	.253	.0579	−32,918	.227	.25	.244	.0777	−32,392	.319
.50	.511	.0934	−32,069	.183	.50	.492	.1227	−31,575	.249
.85	.879	.1342	−31,418	.153	.85	.848	.1741	−30,956	.205
1.00	1.041	.1500	−31,225	.150	1.00	1.004	.1942	−30,763	.193
Part 2. 1 Mole of glycol per liter					Part 4. 10 Moles of glycol per liter				
0.005	0.005	0.0045	−37,478	0.900	0.005	0.005	0.0094	−36,157	1.880
.025	.025	.0131	−35,553	.524	.025	.023	.0253	−34,390	1.109
.050	.050	.0209	−34,728	.418	.050	.047	.0388	−33,624	0.826
.25	.251	.0617	−32,811	.246	.25	.236	.1048	−31,856	.444
.50	.507	.0984	−31,972	.194	.50	.476	.1628	−31,072	.342
.85	.873	.1401	−31,335	.161	.85	.821	.2286	−30,472	.272
1.00	1.031	.1577	−31,136	.153	1.00	.972	.2540	−30,283	.261

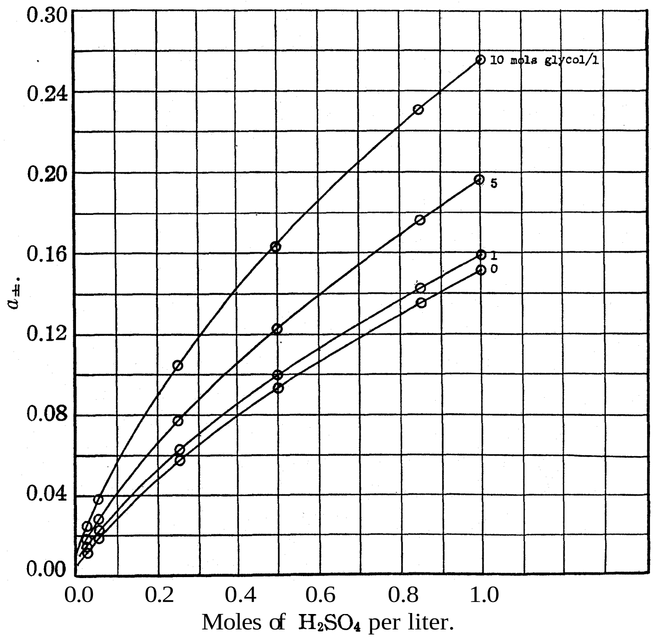

Fig. 4.—Variation of activity with sulfuric acid concentration.

Since A F = −NFE, the free energy of the reaction

$$Hz + Hg_2SO_4 \quad 2Hg + H_2SO_4$$

in the presence of glycol may be calculated by the equation

$$AP = -2 \times 23{,}074\ [0.5724 - (0{,}0600 - 0.00052\,G)\log_{10} N] \qquad (7)$$

These free energy values are set forth in column 5 of Table VI. The calculated values of a, and A F for solutions containing 1 mole of sulfuric acid per liter are somewhat in error since the equations apply only up to about a concentration of 0.85 mole of sulfuric acid per liter. The trend of the free energy of the reaction as glycol is substituted for water may be seen from these values. For the sake of completeness, values of γ are set forth in the last column of Table VI.

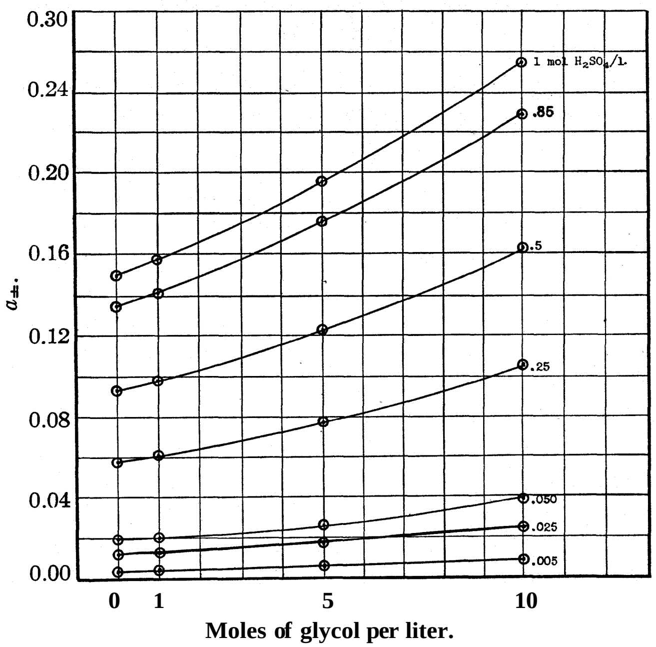

Fig. 5.—Variation of activity with added glycol.

In Fig. 4 the variation of activity with concentration of sulfuric acid for each of the concentrations of glycol is shown. 'In Fig. 5 the variation of activity with concentration of glycol for each of the concentrations of acid is shown. As will be seen, the variation of activity of the acid which is brought about by substituting glycol for water is normal and regular in every way.

Summary

The activity of sulfuric acid in the system H_2SO_4–H_2O–$C_2H_4(OH)_2$ has been studied up to 1 mole of acid and 10 moles of glycol per liter. A new method for calculating activities in such solutions has been presented. The activity of sulfuric acid has been found to vary regularly with change in the concentration of glycol present. Abnormalities in the inversion of sucrose in the presence of ethylene glycol, as catalyzed by sulfuric acid, cannot be attributed to abnormal variations in the activity of the acid in the presence of glycol.

STILLWATER, OKLAHOMA
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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, SCHOOL OF PUBLIC HEALTH, HARVARD UNIVERSITY]

A Rapid Micro Method for the Determination of Chlorides in Fluids

BY LAWRENCE T. FAIRHALL AND J. WILLIAM HEIM

The following method of chloride determination was devised especially for the analysis of very small amounts of fluids and in particular those of biological importance. Certain body fluids, such as peripheral lymph, or the blood of very small animals, or of insects, can be obtained only in such small quantities that analyses hitherto have been very difficult or out of the question.

A necessary step in the volumetric determination of chlorides by means of silver nitrate is that of exactly estimating the excess of silver used in precipitation. Field[1] in 1860 employed iodine dissolved in potassium iodide solution using starch for the end-point, having first neutralized the excess of nitric acid in the solution. King[2] reduced the amount of nitric acid (which interferes with the starch end-point), filtered the silver chloride suspension and titrated the filtrate with potassium iodide solution, using sodium nitrite to oxidize the excess of iodide. McLean and Van Slyke[3] using the same procedure considerably sharpened the end-point by the introduction of a buffer salt--sodium citrate. In the iodimetric method, as in the Volhard method, it is necessary to filter the excess of silver nitrate from the precipitated silver chloride, before completing the titration with potassium iodide; otherwise the latter reacts with the solid silver chloride. For very exact work it has also been shown[4] that it is necessary to remove the precipitated silver iodide just before the end-point is reached, as otherwise the latter is obscured.

The filtration and washing are not only time-consuming but so dilute the sample that for very small amounts of chloride the accuracy is diminished. This step has been eliminated in the following method by carrying out the

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(1) Field, Chem. News, 2, 17 (1860).
(2) Ring, Merck's *Rept.*, 18, 57 (1909).
(3) McLean and Van Slyke, THIS JOURNAL, 37, 1128 (1915).
(4) Lamb and Fairhall, *ibid.*, 45, 390 (1923).

entire analysis in a single 15-cc. centrifuge tube and centrifuging out the silver chloride and the silver iodide at the appropriate points. The silver halide forms a hard, compact mass at the tip of the centrifuge tube, presenting but little surface, and gives no evidence of interference with the end-point in periods of time much in excess of that required for completion of the titration. Therefore no extra manipulation or washing is required and the analysis may be carried to completion in the one tube without transference.

Exact volume measurements of the small amounts of fluid or of the solutions used constitute a necessary step in the procedure and were made by means of extremely fine bore capillary pipets made from thermometer tubing of 0.3–0.5 mm. internal diameter. These pipets are easily made by blowing a bulb in the middle of a convenient length of this tubing and calibrating between two points. One end of the tube should be drawn out to a fine point. By using a fine tip the usual tendency to wet the outside of the tube by the creeping back of liquid was avoided. Typical sampling pipets had volumes of 0.0738 cc. and 0.1106 cc. The silver nitrate solution was also measured from a special pipet of about 1-cc. volume which was provided with a three-way capillary stopcock and a reservoir. A calibrated microburet of 5-cc. capacity was used for titration with the potassium iodide solution.

Fluids containing protein may be directly analyzed for chloride content by first precipitating the protein with tungstic acid and centrifuging. The usual reagents are then added to the supernatant fluid without disturbing the precipitate. This procedure considerably simplifies the analysis of such fluids as blood and lymph.

Method of Analysis

The method finally adopted is as follows. To a 15-cc. centrifuge tube add about 0 5 cc. of water and introduce the sample (about 0.1 cc) using the accurately calibrated sampling pipet for this purpose. Wash the sides of the tube with a little water and stir well with a small stirring rod, which is left in the tube. Add 1 cc. of tungstic acid protein precipitant (when the tungstic acid reagent becomes cloudy it must be discarded) and stir thoroughly. Remove the stirring rod and rinse with a few drops of water. Again wash the sides of the tube with water and centrifuge at high speed for three or four minutes. The precipitated proteins will be thrown down as a firm mass in the case of serum or blood, leaving a water-clear supernatant liquid. Add an accurately measured excess of silver nitrate solution (about 1.5 cc. of silver nitrate solution, 1 cc. of which is equivalent to I mg. of sodium chloride and which contains 250 cc. of nitric acid per liter of solution). Shake the contents of the tube gently to ensure thorough mixing and centrifuge at high speed for two or three minutes. The silver chloride will be thrown onto the protein precipitate as a fine, compact layer. From the microburet add standardized potassium iodide solution (half the equivalent strength of the silver nitrate solution) to within a few drops of the end-point. Thoroughly mix and add I cc. of nitrite–citrate buffer (20 g. of sodium nitrite and 446 g. of sodium citrate per liter of solution) and starch paste. Centrifuge for a minute or so at high speed. The silver iodide will be thrown out, leaving a clear supernatant liquid. Unless the bulk of silver iodide is so removed at this point, it obscures the end-point. Continue the titration to that point at which the first faint permanent color appears when looking down through the tube. The tube may be stoppered and gently inverted to ensure thorough mixing at this last stage of titration without disturbing the precipitate While in the centrifuge it is well to keep the tubes capped on all occasions in order to prevent contamination with chloride bearing dust. Once the solutions are accurately adjusted and the apparatus calibrated, the actual analysis of blood serum or of lymph requires but fifteen or twenty minutes.

Determinations of known amounts of pure potassium chloride by this method and comparison with the similar macro volumetric method involving filtration and washing gave excellent **results.** Analyses were also made of serum, of whole blood and of serum to which known amounts of potassium chloride had been added. These results are shown in Table I.

TABLE I

SUMMARY OF ANALYSES

Material	Normality of $AgNO_3$ soln.	No of analyses	Cl present, mg.	Max. error, %	Av. error, %	Av. deviation, %
Pure KCl	0.03418	20	0.71–0.45	−2.7	−0.07	0.74
Pure KCl	.01709	4	0.30	−2.7	−2.1	.60
Serum	.01709	7	0.31	−2.3	−0.6	.15
Serum + 0.3 mg. KCl	.01709	10	0.61	−2.8	−1.8	1.4
Whole blood	.01709	13	0.31–0.37	−4.5	−1.3	2.5

It is apparent that in 20 determinations of pure potassium chloride ranging in amount from 0.71 to 0.45 mg. the average error was −0.07% with a maximum error of 2.7%, while in four determinations of a smaller amount of potassium chloride (0.30 mg.) the average error was −2.1%, with a maximum error of −2.7%. With serum, serum containing known added amounts of potassium chloride and with whole blood, the average error varied from −0.6 to −1.8%, the maximum error being −4.5% in the case of one of the whole blood analyses. The average error of all the analyses was −1.3%.

Summary

A rapid micro method for the determination of the chloride content of biological or other fluids is described, With this method it is possible to determine a fraction of a milligram of chloride in 0.1 cc. of solution with an accuracy of about 2%.

BOSTON, MASSACHUSETTS

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

The Heat Capacity and Entropy of Calcium Oxalate from 19 to 300° Absolute. The Entropy and Free Energy of Oxalate Ion

BY WENDELL M. LATIMER, PHILIP W. SCHUTZ AND J. F. G. HICKS, JR.

The determination of the entropy of oxalate ion is an important step in the program for the evaluation of ionic entropies,[1] since we wish to use its value in obtaining the entropies of a number of positive ions, especially those of the rare earth group. Moreover, it is of interest theoretically, as there are but few simple divalent negative ions.

The heat capacity of $CaC_2O_4 \cdot H_2O$ was measured directly from 19.31 to 300°K. using the experimental method described by Latimer and Greensfelder.[1c] The heat of solution and free energy of solution were calculated from solubility data. The entropy of calcium ion was calculated from existing data.

Material.—The calcium oxalate used was prepared by precipitation

TABLE I

HEAT CAPACITY OF $CaC_2O_4 \cdot H_2O$

Molecular weight, 146.09

T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.
19.31	0.602	81.72	12.218	210.69	28.436
23.16	1.048	87.06	13.178	219.51	29.331
26.12	1.628	91.54	13.948	224.66	29.619
27.21	1.813	97.28	14.922	228.12	29.953
28.99	2.153	101.36	15.626	232.52	30.086
30.10	2.334	105.74	16.314	236.58	31.063
33.72	3.006	111.25	17.150	241.26	30.732
37.76	3.819	117.98	18.043	247.18	32.138
40.55	4.191	123.74	19.087	249.39	31.593
44.95	5.045	128.81	19.834	256.82	32.182
49.22	5.886	133.99	20.182	257.39	32.561
52.41	6.495	138.95	20.800	264.60	33.424
52.96	6.616	144.15	21.363	267.20	33.524
55.64	7.123	149.34	22.194	272.12	33.780
59.87	7.938	154.90	22.858	275.43	34.108
63.31	8.658	160.69	23.500	281.39	34.722
65.75	9.163	165.55	24.190	283.10	36.329
68.81	9.723	173.23	24.860	291.41	36.082
72.13	10.471	180.71	25.703	299.23	36.537
76.53	11.300	194.87	27.226	299.78	36.418

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(1) For the general theory and previous determinations see (a) Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926); (b) Latimer, *ibid.*, 48, 2868 (1926); (c) Latimer and Greensfelder, *ibid.*, 60, 2202 (1928); (d) Latimer, *J. Phys. Chem.*, *31*, 1267 (1927); (e) Latimer and Kasper, THIS JOURNAL, 61, 2293 (1929); (f) Greensfelder and Latimer, *ibid.*, **50**, 3286 (1928); (g) Latimer and Ahlberg, *ibid.*, **52**, 549 (1930); (h) Latimer and Ahlberg, *Z. physik. Chem.*, Abt. A, 148, 464 (1930); (i) Latimer and Ahlberg, THIS JOURNAL, 64, 1900 (1932).

from calcium chloride solution with ammonium oxalate. The chloride solution was kept at about 70° and the precipitation took place over a period of three days. The reaction mixture was stirred constantly. The precipitated material was washed by decantation until the washings gave no test for chloride with silver nitrate. This washed material was dried at 105° and the dried product showed 100.007% $CaC_2O_4 \cdot H_2O$ on the basis of oxide formed on ignition. Specific heat measurements were made on a sample weighing 73.50 g.

Measurements.—The molal heat capacity values fall on a smooth curve up to 200°K. and deviate only slightly above that temperature. The experimental data are given in Table I and are shown graphically in Fig. 1. The temperature intervals employed in various regions were as follows: 19 to 30°K., about 3° per run; 30 to 200°K., about 5° per run; above 200°K., from 5 to 8° per run.

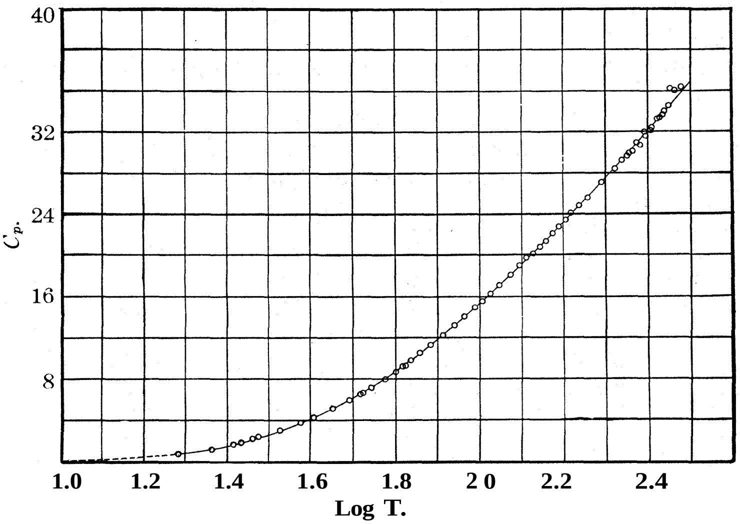

Fig. 1.—Molal heat capacity of calcium oxalate.

Entropy of Calcium Oxalate.—The entropy of calcium oxalate was obtained by a graphical integration of the expression $S = \int_0^T C_p \, d \ln T$ using the curve shown in Fig. 1. The curve below 19.31°K. was extrapolated by means of the Debye T^3 rule. A summary of the entropy calculations is given in Table II.

TABLE II

ENTROPY OF CALCIUM OXALATE

0–19.31°K.	Extrapolation	0.08 E. U.
19.31–298.1°K.	Graphical	37.20 E. U.
Entropy of calcium oxalate at 298.1°K.		37.28 E. U.

Heat of Solution.—The heat of solution of calcium oxalate was calculated from the solubility–temperature coefficient data of Kohlrausch[2] by means of the relation $\Delta H = -R\frac{d\ \ln K}{d(1/T)}$. The solubility product, K, was evaluated from the molal solubility and the activity coefficient, γ, calculated from the Debye–Hückel expression $-\log \gamma = cz^2\sqrt{\mu}$. The factor c has the values 0.505 at 25° and varies as $(TD)^{-3/2}$, where T is the absolute temperature and D the corresponding dielectric constant. Fosbinder[3] finds this expression for log γ to hold for calcium sulfate up to a molality of 0.01. The solubility of calcium oxalate at 25° is 4.85 $\times 10^{-5}$ mole per liter,[2] and the hydrolysis is negligible at this concentration. This calculation leads to a value of 5087 calories for ΔH. The data are shown graphically in Fig. 2a. Holleman[4] and Aumeras[5] give the same values for the solubility at 18 and 20°, respectively, as does Kohlrausch.

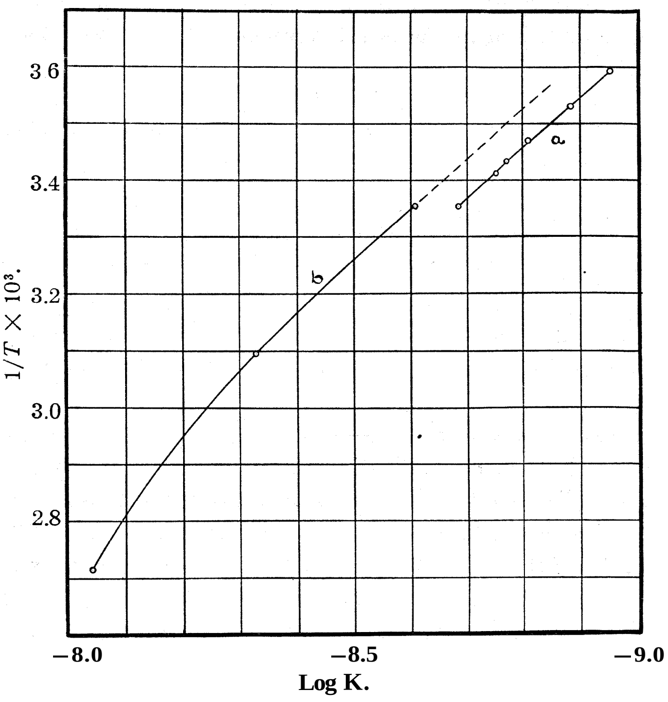

Fig. 2.—Solubility of calcium oxalate.

Assuming the three values given by Richards, McCaffrey and Bisbee[6] to constitute a smooth curve, as shown in Figure 2b, the slope of this

(2) Kohlrausch, Z. physik. Chem., 64, 168 (1908).

(3) Posbinder, THIS JOURNAL, 51, 1345 (1929).

(4) Holleman, Z. physik. Chem., 12, 129 (1893).

(5) Aumeras, J. chim. phys., 24, 43 (1927).

(6) Richards, McCaffrey and Bisbee, Z. anorg. Chem., 28, 71 (1901).

curve at 25° is the same as that of the curve obtained from Kohlrausch's data, thus giving the same value for the heat of solution.

Free Energy of Solution.—The free energy of solution was calculated from the above data, using the expression $AF^O = -RT \ln K$. The values obtained were 11,740 calories (Richards and co-workers) and 11,843 calories (Kohlrausch). The mean of these gives 11,791 calories as the value of AF^O.

Coupled with the heat of solution above this gives for the entropy of solution of calcium oxalate:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{5087 - 11{,}791}{298.1} = -22.5$$

Entropy of **Oxalate** Ion.—Using this value for the entropy of solution, the entropy of the solid as given above and the entropy of water 16.9, as calculated by Giauque,[7] we have for the sum of the entropies of calcium and oxalate ions, 37.28 − 22.5 − 16.9 = −2.12.

In order to determine the entropy of the oxalate ion in respect to $H^+ = 0$, the data summarized in Table III were used to evaluate the entropy of the calcium ion.

TABLE III

THE ENTROPY OF IONIZATION OF WATER AND THE ENTROPY OF CALCIUM HYDROXIDE IN AQUEOUS SOLUTION

	Entropy of substance 298.1°K.	*AH* cal.	*ΔF* cal.	*AS* E. U.	Sum of ionic entropies, *E.* U.
H_2O	16.9[7]	13,329[8]	19,122[9]	−19.43	− 2.53
$Ca(OH)_2$	18.24[10]	−3,385[9]	6,960[9]	−34.7	−16.5

From these values the entropies referred to $S^0{}_{H^+} = 0$ are: OH^-, −2.53 and Ca^{++}, −11.4. Using the sum of the entropies of calcium and oxalate ions as given above, we have for the oxalate ion $S^\circ_{298.1} = 11.4 - 2.1 = 9.3$ E. U.

Free Energy of **Oxalate** .Ion.—Roth and Eyemann[11] give −28,110 calories for the heat of neutralization of oxalic acid. Using this with the "Critical Tables" value for the heat of formation of the aqueous acid and Rossini's^S heat of ionization of water and correcting to 298.1°K. we have

$$H_z + 2C(g) + 2O_2 = 2H^+ + C_2O_4^= \quad A\,H = -195{,}000 \text{ calories}$$

Using the entropies H_2, 31.2;[12] C (graphite), 1.3;[13] O_2, 49.0;[14] H^+, 0 and $C_2O_4^=$, 9.3, we calculate A S = 9.3 − 31.2 − 2.6 − 98.0 = −123.

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(7) Giauque, to be published in *Phys. Rev.*

(8) Rossini, Bur. *Standards J. Research*, 6,847 (1931). The values for *AH, AF* and *AS* for water refer, of course, to the reaction, $H_2O(l) = H_- + OH^-$, and for $Ca(OH)_2$ to $Ca(OH)_2(s) = Ca_{++} + 2OH^-$.

(9) "International Critical Tables." The *AH* of solution fot $Ca(OH)_2$ has been corrected to 298.1, using Rossini's value for $\bar{C}_p$ of OH^- and a calculated value of 14 cal./deg. for Ca^{++}. See Rossini, *Bur. Standards J. Research,* **7**, 47 (1931).

(10) Nernst and Schwers, *Sitzb. Akad. Wiss., Berlin,* 366 (1914); Koref, *Ann. Physik,* [4] *36,* 61 (1911); Ewald, *ibid.,* [4] 44, 1213 (1914). Heat capacity data were obtained from these sources and the entropy calculated by the method used for calcium oxalate above.

(11) Roth and Eyemann, Z. *physik. Chem., 143,* 321 (1929).

(12) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(13) Lewis, Gibson and Latimer, *ibid 44,* 1008 (1922).

(14) Giauque and Johnston, *ibid.,* **51**, 2300 (1929).

With the heat of reaction as given above, this gives $AF^\circ = -195{,}000 + (298.1 \times 123) = -158{,}000$ calories for the free energy of formation of oxalate ion.

Summary

The specific heat of $CaC_2O_4 \cdot H_2O$ has been measured from 19 to 300°K. and the entropy of the salt determined by graphical integration. Coupling this value with the entropy of solution and the entropy of calcium ion as herein calculated, the entropy of oxalate ion has been determined. A value for the free energy of oxalate ion has been calculated.

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS UNIT OF THE BUREAU OF CHEMISTRY AND SOILS]

Solubility of Nitrogen in Liquid Ammonia at 25° from 25 to 1000 Atmospheres

BY R. WIEBE AND T. H. TREMEARNE

Very few measurements have been made on the solubility of gases in liquid ammonia. The most extensive were made by Larson and Black[1] on the solubility of a 3 : 1 hydrogen–nitrogen mixture over a temperature range from -25 to $+22°$ and up to 150 atmospheres. A rough incidental measurement of the solubility of hydrogen in liquid ammonia at $-70°$ was made by Schlubach and Ballauf.[2] Aside from the practical importance, the knowledge of solubilities is of importance for any theory of solutions.

Apparatus and Procedure

Figure 1 shows the apparatus. Synthetic ammonia was fractionated and the middle portion was condensed into steel cylinder A of about 1400 cc. capacity. Nitrogen at a pressure somewhat in excess of the final equilibrium pressure was introduced and the steel cylinder after being disconnected, was shaken by means of the eccentric D. The shaking motion was stopped after a few hours and the pressure was adjusted to the final value through C which was connected both to the piston gage and the compression system. The apparatus was then shaken at this pressure and if necessary the procedure was repeated, until equilibrium was established as indicated by no further pressure change. Several independent sets of runs were taken at each pressure. No trend was observed in the results, showing that equilibrium must have been reached.

The receiving apparatus was evacuated up to the mercury seal maintained in the capillary between G and the buret system H. E was immersed in liquid air. Valve B was then opened slightly, permitting a mixture of ammonia and nitrogen to enter the receiving apparatus. The ammonia was condensed in E and the nitrogen expanded into the Toepler pump. When the sample was considered to be sufficiently large, valve B was closed and the Toepler pump G was operated in order to transfer the nitrogen into

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(1) Larson and Black, Ind. *Eng.* Chem., 17, 715 (1925).

(2) Schluhach and Ballauf, *Ber.*, 54, 2825 (1921).

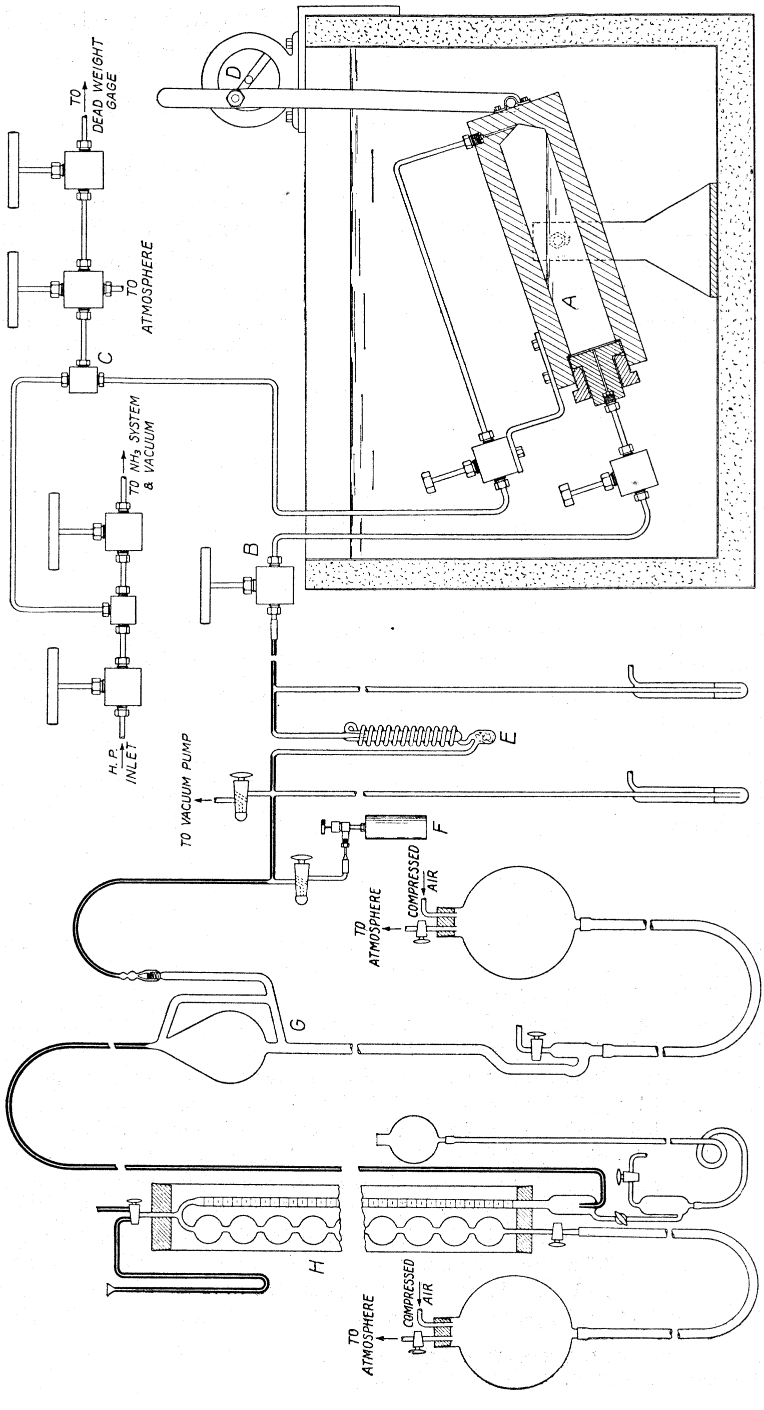
TO DEAD WEIGHT GAGE
D
TO ATMOSPHERE
A
C
TO NH$_3$ SYSTEM & VACUUM
B
H.P. INLET
E
TO VACUUM PUMP
F
COMPRESSED AIR
TO ATMOSPHERE
G
H
COMPRESSED AIR
TO ATMOSPHERE

Fig. 1.

the buret system H. The gas was measured partly in a 12-bulb buret, each bulb having a volume of approximately 25 cc., and the excess in a 50-cc. straight buret, Mercury was used exclusively.

The steel cylinder F, having a weight of approximately 190 g., was used to collect the ammonia through distillation from E. The steel cylinder was weighed empty before and after each measurement; the difference was ordinarily less than 2 mg. The average of the two values was used. Since in most cases the weight of ammonia ranged from 4 to 5 g., this uncertainty amounted to less than 0.05%. Small amounts of ammonia were carried through trap E by the nitrogen. These traces were later recovered by absorption in water and determined by titration. This correction was of importance at the lowest pressures where the total amount of gas was small; at higher pressures the correction was ordinarily less than 0.5%.

Pressures were measured by means of two piston gages described by Bartlett and co-workers.[3]

The nitrogen was 99.9% pure, the impurities being argon and traces of oxygen. The water content of the ammonia was 0.07%.

The apparatus was tested by measuring the solubility of nitrogen in water at 100, 200 and 300 atmospheres and 25°. The agreement with known values was within about a tenth of one per cent.[4]

Discussion of Results

Table I and Fig. 2 give a summary of the results.

TABLE I

Total pressure	Number of runs	Solubility in cc. of nitrogen (S. T. P.) per g. of ammonia
25	21	2.22
50	13	5.73
100	6	12.04
200	8	22.48
400	19	37.02
600	10	45.43
800	21	51.10
1000	16	54.83

The error is estimated to be several tenths of one per cent. and may be of the order of one per cent. at the lowest pressure. Sources of error were the impurities in nitrogen and ammonia, uncertainties in calibration, weighing, titrating and possibly changes in solubility due to slight pressure fluctuations during the run.

As will be noted from the curve in Fig. 2, zero solubility is attained close to ten atmospheres total pressure. The vapor pressure of liquid ammonia at 25° is 9.8955 atmospheres.[5]

Results for the amount of gas dissolved at any particular partial pressure of nitrogen could not be given for lack of adequate equations of state at the high pressures used.

(3) Bartlett, Cupples and Tremearne, THIS JOURNAL, 60, 1275 (1928).

(4) The values so obtained were published by Wiebe, Gaddy and Heins, *Ind. Eng* Chem., 24, 927 (1932).

(5) Cragoe, Meyers and Taylor, Bur. of Standards Scientific Paper No. 369 (1920); also THIS JOURNAL, 42, 206 (1920).

Lurie and Gillespie[6] have calculated the equilibrium pressure of ammonia in a nitrogen–ammonia mixture using an equation of state for mixtures up to 60 atmospheres total pressures and found satisfactory agreement with their composition measurements. Randall and Sosnick[7] applied the generalized Raoult's law[8] to gaseous solutions. They found that for solute gases below their critical temperature, the method led only to rough quantitative results and would therefore be of little use in this work.

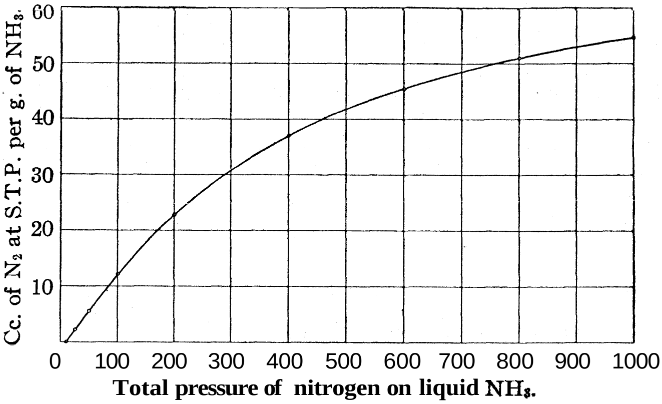

Fig. 2.

The authors are indebted to Mr. W. L. Edwards for the design of the shaking apparatus.

Summary

A satisfactory high pressure apparatus for measuring solubilities of gases in liquids having high vapor pressures has been described.

The solubility of nitrogen in liquid ammonia at 25° and from 25 to 1000 atmospheres has been determined.

Washington, D. C.

Received September 22, 1932
Published March 7, 1933

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(6) Lurie and Gillespie, This Journal, 49, 1146 (1927).

(7) Randall and Sosnick, *ibid.*, 50, 967 (1928).

(8) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 222.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A Study of the Reactions of Free Ethyl Radicals from the Thermal Decomposition of Tetraethyllead[1]

BY RICHARD N. MEINERT

It has long been assumed that the thermal decomposition of hydrocarbons of the paraffin series takes place first by the scission of a C–C bond with the formation of free alkyl radicals, followed by the reactions of these radicals with each other or with hydrocarbon molecules to produce olefin and smaller paraffin hydrocarbons.[2] Rice, Johnston and Evering have recently demonstrated the existence of free alkyl radicals obtained by decomposing paraffin hydrocarbons and acetone.[3] In view of the importance now being attributed to free radicals, a study of the reaction products of a wide variety of them reacting with each other in the absence of other substances, so far as this is possible, is desirable. For if the thermal decomposition of hydrocarbons consists of splitting into radicals which then react to form the final products, a study of the reactions of the radicals themselves should throw considerable light on the mechanism of hydrocarbon decomposition. Certain of the metal alkyls offer an interesting possibility for such a study. This is especially true of the lead alkyls since Paneth and his co-workers have demonstrated that both tetramethyl- and tetraethyllead break down when heated to produce free radicals.[4] Rice and his co-workers have shown that the free radicals obtained from the lead tetra-alkyls have identical properties with those obtained by the thermal decomposition of hydrocarbons and acetone.[3] A special advantage is obtained by using the lead alkyls to produce the free radicals because they decompose at temperatures considerably lower than those at which hydrocarbons decompose, that is, at which rupture of a C–C bond occurs. Hence by the low temperature decomposition of tetraethyllead, free ethyl radicals may be obtained and their reactions studied without the possibility of decomposition occurring within the radicals themselves.

The thermal decomposition of tetramethyllead has been studied by Simons, McNamee and Hurd, who report that two sets of reactions occur, one set taking place on the walls of the reaction vessel, the other in the homogeneous gas phase.[5] Geddes and Mack studied the thermal decomposition of tetraethylgermanium, their interest being centered upon the rate of the decomposition rather than upon the products formed.[6]

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(1) Part of the material contained in this paper was presented at the Buffalo meeting of the American Chemical Society, Sept., 1931.

(2) See (a) Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co.. 1929; (b) Rice. THIS JOURNAL, **53**, 1959 (1931).

(3) Rice, Johnston and Evering, ibid., 54, 3529 (1932)

(4) (a) Paneth and Hofeditz, *Ber.*, 62, 1335 (1929); (b) Paneth and Lautsch, *Nature*, **125**, 564 (1930).

(5) Simons, McNamee and Hurd, J. *Phys. Chem.*, 36, 939 (1932).

(6) Geddes and Mack, THIS JOURNAL, **52**, 4372 (1930).

Taylor and Jones decomposed tetramethyllead, tetraethyllead and diethylmercury in the presence of ethylene. They were studying the effect of free ethyl and methyl groups upon ethylene.[7] Ipatjev, Bogdanov and Razuvaev have investigated the action of hydrogen at high pressures upon tetraphenyl-, tetramethyl- and tetraethyllead.[8]

The present work is an attempt to determine how free ethyl radicals, split off from tetraethyllead, react with each other, by a study of the reaction products. The experiments were carried out under a wide variety of conditions. Liquid tetraethyllead was decomposed at its boiling point; the flow method was used at atmospheric pressure and at low pressure; the static method was used at several temperatures and pressures and in the presence of nitrogen and of Pyrex glass packing. Each of these methods has its advantages and disadvantages. The flow method would appear to be the best for our purpose, for under these conditions the concentrations of tetraethyllead and of the hydrocarbon products are uniform throughout the experiment. These conditions give the best chance of studying the reactions of the free radicals without complicating side reactions. However, the very fact that the concentrations of starting material and of products are constant may serve to mask any effect they might have upon the reactions. The static method would probably show whether or not uniform concentration is an important factor in the results obtained by the flow method, for in the former method the conditions are constantly changing. The disadvantage of the static method is that initially the concentration of tetraethyllead is very high compared to that of the free ethyl groups, and at the end of the experiment the concentration of hydrocarbon products is very high, so that the reactions might change considerably in nature and amount during the course of the heating. The results of experiments by the static method must therefore be regarded as the composite results of a series of reactions which may change in rate more or less uniformly during the course of the experiment.

Experimental

The tetraethyllead used in these experiments was the commercial grade purified by the method recommended by Calingaert.[9] In the experiments made by the static method and in those using the flow method at low pressure, the purified material was further distilled in high vacuum at room temperature.

The method of gas analysis used was that given by Hurd and Spence.[10] It was found, in agreement with these authors, that butane was absorbed slowly in the fuming sulfuric acid pipet, along with ethylene. To allow for this, the gas was passed into this pipet several times until a constant amount was absorbed in each passage. A correction was then made to the butane and ethylene percentages. This correction was determined separately for each analysis. In the combustion analysis of the hydrocarbons

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(7) Taylor and Jones, THIS JOURNAL, 52, 1111 (1930).

(8) Ipatjev, Bogdanov and Razuvaev, *J. Russ. Phys.-Chem. Soc.*, *61*, 1791 (1929).

(9) Calingaert, *Chem. Rev.*, 2, 56 (1925).

(10) Hurd and Spence, THIS JOURNAL, 51, 3356 (1929).

of the saturated series, it was found that the average number of carbon atoms in the molecule ranged from about 2.5 to 3.5. These gases were calculated as ethane and butane, since it was certain that at the low temperatures used in the experiments the butane formed in the reaction would not decompose to form either propane or methane, neither would these gases be expected to form from the free ethyl radicals. To justify this assumption, several samples of the gaseous reaction products were fractionated by means of liquid air, and an acetone and solid carbon dioxide mixture, into three fractions which were analyzed separately. The combined results of the separate analyses were compared with the analysis of the original sample, and agreed closely in each case. No detectable amounts of methane or propane were found.

Decomposition of Liquid Tetraethyllead at its Boiling Point.—It is reported in the literature by several workers that tetraethyllead boils at about 220° with decomposition. Experiments to determine the products of this decomposition were performed. The apparatus consisted of a 50-cc. round-bottomed flask with a neck 50 cm. long to serve as a reflux column. The apparatus was filled with nitrogen, five cubic centimeters of tetraethyllead introduced, and the system pumped out and then filled with nitrogen several times in order to eliminate oxygen from the apparatus. The flask was then fitted with a delivery tube extending under water into a two-liter bottle which served to collect the gases. The flask was heated gently with a luminous Bunsen flame so that the liquid was kept just at the boiling point, with no visible refluxing. In making the first run, the heating was apparently too rapid, as a mild explosion resulted after about 500 cc. of gas had been collected. With more careful heating, two runs were made in which all of the tetraethyllead was decomposed. A deposit of finely divided lead was left in the flask. . This deposit was easily removed with nitric acid; no evidence of the presence of carbon was detected. The data obtained are given in Table I. It is apparent that most of the ethyl groups have reacted to form ethane and ethylene, with only a small amount of butane. This is in marked contrast to the products formed when the decomposition takes place in the vapor phase, as the results below will show.

TABLE I

PRODUCTS OBTAINED FROM THE THERMAL DECOMPOSITION OF LIQUID TETRAETHYLLEAD

	Run 1	Run 2
Time of run, min.	32	40
Grams of $Pb(C_2H_5)_4$ used	8.25	8.25
Cc. of gas obtained	1780	1885
ANALYSIS OF GASES, %		
Ethylene	41.0	40.6
Ethane	52.7	52.5
Butane	3.6	4.9
Hydrogen	0.5	0.2
Butylenes	2.1	1.8
H/C ratio in gases	2.54	2.54

Decomposition of Tetraethyllead by the Flow Method.—The flow method was used to decompose tetraethyllead in the vapor phase, both at atmospheric pressure and at a pressure of one millimeter.

In the experiments at atmospheric pressure, the reaction tube was of heavy Pyrex glass, 20 mm. inside diameter and 40 cm. long. This tube was placed in a specially constructed tube furnace at an angle of about 20" to the horizontal. A buret was sealed by means of deKhotinsky cement to a 12-cm. length of 10-mm. tubing sealed to the upper end of the furnace in a vertical position. A trap kept in ice water was sealed onto the lower end of the reaction tube and served to collect any liquids which were carried over by the gases. The side arm of the trap was connected to a manometer and to a 12-liter bottle in which the gases were collected. This bottle had a leveling device so that the pressure inside the system could be kept constant. The temperature of the furnace was measured by a thermocouple placed alongside and in contact with the reaction tube at the center of the furnace.

Before making a run the system was pumped out with an oil pump for half an hour, after which dry nitrogen was admitted. The apparatus was again pumped out and nitrogen admitted, this procedure being carried out several times in order to remove all oxygen. The furnace was heated to the desired temperature and maintained there for half an hour before beginning the run in order to insure a steady thermal state. Lead tetraethyl was dropped slowly into the reaction tube from the buret. The buret reading, the gas volume and the temperature were recorded at five-minute intervals, thus making it possible to keep the rate of the decomposition uniform. The liquid tetraethyllead was quickly vaporized in the hot tube. It was apparent that the substance could be vaporized without decomposition if the amount present at any one time was small and the rate of vaporization rapid. Furthermore, the vapors were found to be far more stable than the substance in the liquid form. This is shown by the fact that even when the furnace temperature was 325°, an appreciable amount of the tetraethyllead vapor passed unchanged through the reaction tube and was condensed in the trap. During the experiment, the decomposition was smooth and uniform. Lead was deposited loosely on the sides of the tube, and small amounts in the form of fine dust were carried over by the gases and settled out in the trap. The results of a number of runs made by this method are given in Table II. Run number 7 was made with the reaction tube packed with small pieces of Pyrex glass so that the surface to volume ratio was increased about tenfold. There were small amounts of liquid products mixed with the undecomposed tetraethyllead found in the trap in runs three, five and one. These liquids were present in amounts too small to identify, but it was observed that a portion of them boiled from 0 to 30° and a portion from 30 to 50°. They had an odor resembling that of petroleum ether. Only traces of these liquids were formed above 375°.

TABLE II

PRODUCTS FROM THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD USING THE FLOW METHOD AT ATMOSPHERIC PRESSURE

Run number	3	5	1	4	2	6	7[a]
Temperature of furnace, °C	300	325	375	425	450	475	425
Time of run, min.	105	65	95	70	60	45	23
Grams of $Pb(C_2H_5)_4$ used	24.3	17.3	56.9	49.5	47.4	39.6	18.4
Cc. of gas obtained	1750	2015	9455	9500	9545	8330	3650
ANALYSIS OF GASES, %[b]							
Ethylene	12.0	11.4	24.8	29.4	31.3	31.2	32.3
Ethane	46.1	41.9	26.0	20.5	17.3	19.1	18.2
Butane	34.6	34.9	32.7	35.7	36.8	34.6	35.5
Hydrogen	5.8	8.1	11.4	11.1	12.4	12.1	12.5
Butylenes	1.6	3.7	5.1	3.2	2.2	3.0	1.5
Liquid products, cc.	1–2	1–2	trace	trace	trace	trace	trace
% Decomposition, approx.	34	55	76	89	93	96	89
H/C ratio in gases	2.66	2.65	2.56	2.53	2.52	2.52	2.53

[a] The tube was packed with Pyrex glass. [b] The system was full of nitrogen at the start of the run and of reaction products at the end of the run. The analyses were calculated on a nitrogen free basis to compensate for the gases remaining in the tube.

The percentage decomposition given in the table is approximate and was calculated from the amount of tetraethyllead used in the run and the carbon and hydrogen content of the gaseous products.

Examination of the data in Table II shows that the amount of butane in the gaseous products is very nearly the same at all temperatures, while the ethane and ethylene content changes very markedly. The ratio of ethane to ethylene at the low temperatures is four to one, while at higher temperatures it is about two to three. This increase in the amount of ethylene formed cannot be due to the pyrolysis of ethane or butane since they are both stable at temperatures used in the experiments.[2a] Furthermore, the ratio of ethylene to hydrogen is roughly constant at all temperatures and is 2.5 to 1 rather than 1 to 1. There is therefore a definite tendency to form ethylene rather than ethane at high temperatures, which is in agreement with the relative stabilities of the two gases. The fact that liquid products are more abundant at low than at high temperatures is also significant, for Taylor and Jones have reported that free ethyl groups cause the polymerization of ethylene.[7] These liquid products may be formed by the polymerization of ethylene, induced by the presence of the free ethyl groups. The polymerization evidently occurs more readily at low than at high temperatures. The polymerization of ethylene may account also for the small amounts of butylene found among the gaseous products.

A comparison of runs 4 and 7 shows that increasing the surface area in the reaction tube has practically no effect upon the course of the reaction.

The ratio of hydrogen to carbon atoms in the gaseous products indicates clearly that at low temperatures some of the ethyl radicals abstract hydrogen either from other radicals or from tetraethyllead molecules, consequently producing a large amount of ethane and leaving a deficiency of carbon atoms in the gaseous products. There was some carbon actually deposited in the reaction tube at low temperatures. Above 375°, the H/C ratio is very closely 5 to 2, showing that the reaction proceeds without this effect. These observations are in agreement with the results found by Simons, McNamee and Hurd for tetramethyllead.[5]

Flow Method at Low Pressure.—In order to use the flow method at low pressure it was necessary to pump the vapor of tetraethyllead through a hot tube by means of a high speed pump capable of reaching low pressures and of allowing the gas pumped off to be collected. An automatic Sprengel pump was built but proved to be too slow for the purpose. However, the Sprengel pump, operating to maintain a pressure of less than a millimeter, provided a good fore pump for a mercury vapor pump, which had the necessary speed. The mercury vapor pump operated below 100° so that no decomposition took place in the pump.

The apparatus consisted of several small bulbs sealed onto a manifold of 10-mm. tubing which was connected by means of a 2-cm. length of 1-mm. capillary tubing, which served to minimize backward diffusion of the gases, to a U-tube of 4-mm. tubing. The U-tube was 12 cm. in length and was placed inside a small electric furnace. From the U-tube a connection led to the mercury vapor pump, which in turn was directly connected to the Sprengel pump, where the gases were collected. The apparatus was built entirely of Pyrex glass, and was thoroughly flamed and pumped out to a pressure of 10^{-6} mm. before using.

A seal on the first bulb was opened, a quantity of tetraethyllead introduced, and the seal again closed. The system was then pumped out, keeping the bulb and contents at −78°. The tetraethyllead was then fractionally distilled at room temperature, using the cold bath to condense the vapor in the additional small bulbs. The middle fraction was retained, the other bulbs being sealed off. After the system had been pumped out again, it was ready for a run. The furnace was heated to 500°, the pumps started and the tetraethyllead reservoir warmed up to 30° with a water-bath. The gases were pumped off at the rate of about 5 cc. (0°, 760 mm.) per hour, and calculation showed that the time of passage through the hot tube averaged slightly less than one second. The pressure in the system was 0.5 mm. Examination of the U-tube at the end of the run showed that most of the decomposition took place in the first fourth of the tube, the walls there being covered with a smooth deposit of lead. The free ethyl groups therefore had ample time to react with each other before they left the reaction chamber, for both Paneth and Rice have determined the half-life period of the free groups to be of the order 10^{-3} seconds.[2b,4] The data for the experiments are given in Table III.

TABLE III

PRODUCTS FROM THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD USING THE FLOW METHOD, PRESSURE 0.5 MM.

Run number	1	2
Time of run, hours	10	12
Furnace temperature, °C.	500	500
Cc. of gas obtained	49.8	54.4
ANALYSIS OF GASES, %		
Ethylene	33.7	32.3
Ethane	17.8	20.7
Butane	34.1	32.3
Hydrogen	14.3	14.3
Butylenes	0.2	0.5
H/C ratio in gases	2.55	2.57

It will be observed that these results are very much the same as those obtained by the flow method at atmospheric pressure when the temperature was above 450°.

Decomposition of Tetraethyllead by the Static Method.—The procedure used was similar to that used by Simons, McNamee and Hurd in decomposing tetramethyllead by the static method.[5] A series of glass bulbs having a thin capillary tube sealed to the bottom were sealed onto a manifold. Several smaller bulbs for the distillation of the sample were sealed to the same manifold, which was then connected by means of a trap to a mercury vapor pump and a McLeod gage. All stopcocks were eliminated by using mercury traps. The system was thoroughly pumped out while being heated, until the pressure remained less than 10^{-5} mm. after standing overnight. A seal was then opened, tetraethyllead introduced into one of the small bulbs and then fractionally distilled at room temperature. The purified sample was distilled into the capillaries of the larger bulbs to a predetermined level and the bulbs were sealed off and heated in a furnace. After the heating, a file mark was made on the thin capillary, which was then sealed into a larger tube, connected with the pumping system in such a way that the tip of the capillary could be broken off by means of a magnetic plunger. The seal was made with deKhotinsky cement. The system having been evacuated, the plunger was allowed to fall and break the capillary, and the gas pumped out and collected by means of an automatic Sprengel pump. The sample of gas was then transferred to the gas analysis apparatus. Experiments were made at several temperatures, and the size of the bulbs was varied from 100 cc. to 500 cc. in order to vary the pressure and still have a sample of gas large enough to analyze. The effects of increased surface in the bulb and of introducing nitrogen were studied. The bulbs were heated in the furnace for different lengths of time, in all cases enough to decompose about 90% of the tetraethyllead in the bulb. The results have been tabulated as far as possible to show the effect of varying the conditions within the bulbs. Table IV shows the effect of temperature and pressure

The first four columns in the table show the effect of varying temperature. A series of 100-cc. bulbs was heated, each at a different temperature and each long enough

TABLE IV

EFFECTS OF TEMPERATURE AND PRESSURE UPON THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD—STATIC METHOD

Bulb number	A-1	A-2	A-3	A-4	B-9	C-7	A-3	A-6	A-9
Capacity (cc.)	110	110	110	103	110	108	110	340	550
Temp. of furnace, °C.	150	200	275	350	275	275	275	275	275
Time heated, hrs.	28	6	2	0.5	3	2.5	2	2	2
$Pb(C_2H_5)_4$ used, g.	0.467	0.436	0.426	0.378	0.841	0.498	0.426	0.452	0.459
Pressure of $Pb(C_2H_5)_4$ vapor at furnace temp.. mm.	345	360	410	442	807	478	410	141	88
Cc. gas obtained	84.0	43.8	58.7	89.5	118	71.0	58.7	634	71.8
ANALYSIS OF GASES, %									
Ethylene	37.8	9.2	5.9	36.2	6.9	6.8	5.9	11.2	14.2
Ethane	45.8	47.3	44.8	19.4	55.8	44.8	44.8	29.2	24.1
Butane	13.6	38.7	44.2	31.4	32 4	41.8	44.2	51.4	52.2
Hydrogen	1.8	2.7	3.6	10.4	1.7	3.5	3.6	5.9	6.7
Butylenes	1.0	2.2	1.4	2.6	3.3	3.0	1.4	2.2	2.9
H/C ratio in gases	2.54	2.64	2.65	2.50	2.73	2.63	265	2.55	2.56

to decompose most of the tetraethyllead. In the case of the first bulb, heated to only 150°, the amount of tetraethyllead in the bulb was so great that it could not all vaporize, since the vapor pressure of $Pb(C_2H_5)_4$ at 150° is only approximately 140 mm., and there was sufficient present in the bulb to give a pressure of 345 mm. at 150" if it were all vaporized. A comparison of the products obtained in this run with the results in Table I indicates that most of the decomposition has taken place in the liquid phase, which is to be expected. In all of the other runs the temperature was high enough to ensure that all of the tetraethyllead would vaporize before the final temperature was reached. It is

TABLE V

EFFECTS OF INCREASED SURFACE AND OF NITROGEN UPON THE THERMAL DECOMPOSITION OF TETRAETHYLLEAD—STATIC METHOD

Bulb number	C-7	C-8	C-5	C-1	C-3	C-4
Capacity of bulb, cc.	105	60	315	220	105	105
Bulb packed	No	Yes	No	Yes	No	No
Pressure of N_2, mm. at 20°	...	...	...	...	251	283
Temp. of furnace, °C.	275	275	275	275	275	275
Time of heating, hours	2.5	2.5	2.5	2.5	2.5	2 5
$Pb(C_2H_5)_4$ used, g.	0.498	0.373	0.574	0.479	0.403	0.393
Pressure of $Pb(C_2H_5)_4$ vapor at furnace temp.. mm.	500	661	192	230	407	397
Cc. gas obtained	71	57	80	70	90	91
ANALYSIS OF GASES, %[a]						
Ethylene	6.8	5.7	8.1	5.5	7.2	5.8
Ethane	44.8	55.1	36.7	44.4	51.9	48.8
Butane	41.8	32.3	46.8	41.7	35.2	39.3
Hydrogen	3.5	4.3	4.8	5.2	2.2	3.1
Butylenes	3.0	2.5	3.6	3.2	3.4	3.1
H/C ratio in gases	2.63	2.70	2.61	2.65	2.66	2.65

[a] The analyses of runs C-3 and C-4 have been calculated on a nitrogen free basis for comparison with the others.

interesting to note that as the temperature increases, the ethylene content of the gases decreases, and the butane content increases until 350°, at which point the ethylene becomes very abundant, the hydrogen increases and the ethane decreases markedly in amount. This will be discussed more fully in a later section. The last five columns of Table IV show the effect of pressure upon the decomposition. High tetraethyllead pressure favors the formation of ethane; as the pressure is lowered, butane becomes the most abundant product. This fact, together with the hydrogen–carbon ratios, shows that at the high pressures some of the ethyl groups form ethane at the expense of the hydrogen atoms of other ethyl groups. This was confirmed by the fact that slight amounts of carbon were formed on the walls of the bulb where the H/C ratio in the gases was high.

A series of runs was made with half the bulbs packed with small pieces of Pyrex glass, the others unpacked. Two runs were made with nitrogen at a pressure of approximately one-third of an atmosphere (at 20") in the bulb. The results of these runs are given in Table V.

Due to the smaller volume in the packed bulbs, the pressure is slightly greater than in the corresponding unpacked bulbs, but a comparison with the results in Table IV will show that the small increase in pressure is not enough to account for the increased amount of ethane formed and the corresponding decrease in the amount of butane. It is evident that one of the reactions responsible for the ethane formation is a wall reaction. Nitrogen as an inert diluent has nearly the same effect as increased surface.

Discussion

In discussing a possible mechanism for the thermal decomposition of tetraethyllead, we shall consider that the molecule first breaks up into a lead atom and free ethyl radicals. This has been assumed by all previous workers in the field and is in complete accord with the experimental results. The discussion therefore resolves itself into an effort to determine what happens to the ethyl groups which are released.

An examination of the products formed under varying conditions indicates four reactions which are involved. We shall state these reactions and proceed to discuss them in the light of the data obtained.

Reaction (1): an ethyl radical may, when the concentration of tetraethyllead is high, extract hydrogen from the tetraethyllead molecule and form ethane. We shall indicate the reaction thus: $C_2H_5 + [H] \longrightarrow C_2H_6$. Reaction (2): two ethyl groups may combine to form butane: $2\ C_2H_5 \longrightarrow C_4H_{10}$. Reaction (3): two ethyl groups may react to form ethylene and hydrogen: $2\ C_2H_5 \longrightarrow 2C_2H_4 + H_2$. Reaction (4): two ethyl groups may react by disproportionation: $2\ C_2H_5 \longrightarrow C_2H_6 + C_2H_4$.

Reaction (1) is of primary importance at high pressures and low temperatures. The percentage of ethane was always very high under such conditions. The ethane percentage in the gaseous products was in some cases four times as great as the ethylene percentage, hence the ethane could not all have been formed by reaction (4), which would produce ethane and ethylene in equal amounts. The reaction is a wall reaction, for the results in Table V show a marked increase in the ethane percentage without a corresponding increase in ethylene when the bulbs were packed so as to increase the surface. The conditions best suited to this reaction are a high concentration of tetraethyllead molecules and a slow rate of decomposition, so that there is a greater chance for an ethyl group to collide with a tetraethyllead molecule than with another ethyl radical. These conditions occur in runs 3 and 5 made by the flow method and in most of the runs made by the static method, particularly in run B-9 where the initial pressure of tetraethyllead vapor was highest. In run A-4, Table IV, the temperature was high, hence the rate of decomposition was rapid and the concentration of ethyl groups high. Consequently the influence of reaction (1) on the products from this run was small, and the percentage of ethane is very low. In runs **A-6** and A-9, the initial pressure of tetraethyllead vapor was low, which also inhibited reaction (1). That this reaction is due to the extraction of hydrogen from a tetraethyllead molecule rather than from one of the hydrocarbon products is made evident by the conditions under which the reaction occurs. Simons, McNamee and Hurd found that a similar reaction occurred with tetramethyllead.[5] They assume that this reaction takes place to a greater extent at low temperatures than at high, because the methyl radicals are released on the wall in the condensed phase when the temperature is low and hence can react easily with adjacent tetramethyllead molecules, while at high temperatures the methyl groups are released mostly in the gas phase and hence can react readily with each other, less readily with other molecules of tetramethyllead. There seems to be no evidence that most of the decomposition occurs on the walls at low temperatures and in the gas phase at higher temperatures. Geddes and Mack have found, on the contrary, that at least in the cases of tetraethyllead and tetraethylgermanium, the decomposition is 98% homogeneous in the gas phase.[6] Of course this tells us nothing about the reactions of the free groups after the decomposition. The difference in the relative importance of this reaction at different temperatures can be satisfactorily explained on the basis of the relative concentrations of the ethyl radicals and tetraethyllead molecules.

Reaction (2) is of interest because it shows definitely that two free ethyl groups can combine to form butane, probably by a wall reaction or by a three-body collision. Paneth, without making a complete analysis of the products of the decomposition, reported that a large fraction of the ethyl radicals was recovered as butane. A similar reaction has been found by Simons, McNamee and Hurd to take place with methyl radicals. The percentages of butane in the products from runs made by the flow method are fairly constant. This is not the case when the reaction is carried out in a sealed bulb, in which case the most apparent fact is that reaction (2) becomes more effective as the initial pressure of tetraethyllead is lowered, and less effective when the surface in the bulb is increased. But these are precisely the conditions which either hinder or favor reaction (1), and an inspection of the data shows that as the butane content of the gaseous products increases, the ethane content decreases, and vice versa. This explains the apparent change in the relative rate of reaction (2) with changes in temperature or pressure when the static method was used. Any factors which cause an increase in the yield by reaction (1) will cause a decrease in the products of reaction (2), due to the depletion of the ethyl radicals. When the flow method was used, the temperature was high, and the concentration of ethyl groups was also high, due to the more rapid decomposition of the tetraethyllead, and the data show very little change in the effectiveness of reaction (2) in determining the end products of the decomposition.

Reaction (3) accounts for a large fraction of the gaseous products particularly when the flow method was used. At the higher temperatures, it accounts for most of the ethylene. The ethylene content is about two and one-half times the hydrogen content—hence reaction (3) produces about 80% of the ethylene. It is probable that this reaction takes place in more than one step. Rice, in discussing the part played by free radicals in the decomposition of hydrocarbons, shows from energy calculations that it is possible for an ethyl group to lose a hydrogen atom thus: $C_2H_5 \longrightarrow C_2H_4 + H$.[11] The hydrogen atom and another ethyl radical could then combine to form a hydrogen molecule and another molecule of ethylene. Both of these reactions might occur when two ethyl groups meet in a collision on the wall.

Reaction (4) occurs to a lesser extent than the others, for most of the ethane can be accounted for by reaction (1) and most of the ethylene by reaction (3). Furthermore, there is no relation between the percentages of these gases such as would be demanded if reaction (4) were the main one. This reaction is prominent in only one case, when the temperature was 350° and the decomposition was rapid and the concentration of ethyl groups at any one instant was high (Run A-4, Table IV). It seems probable therefore that this reaction occurs in the gas phase rather than on the walls. This statement is borne out by Rice's conclusions in his paper on free radicals in thermal decomposition.[11] Rice concludes from a study of the decomposition products of hydrocarbons under various conditions, that a reaction between two ethyl groups to produce ethane and ethylene occurs in a ternary collision, and not to any great extent on the walls. The fact that this disproportionation reaction plays such a small part in the reactions of free radicals throws doubt on some of the mechanisms which have been proposed for hydrocarbon decompositions, which assume that practically all of the radicals formed by the breaking of a C–C bond react by disproportionation to produce an olefin and a paraffin hydro-

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(11) Rice, THIS JOURNAL, 53, 1962 (1931).

carbon. The facts agree rather with Rice's assumption of a chain reaction which is terminated by a ternary collision resulting in disproportionation.

When tetraethyllead is decomposed in the liquid phase, an apparent disproportionation accounts for more than 90% of the total products; but the conditions are very different from those in the vapor phase reaction. The reactions in the liquid phase are undoubtedly more complex than the results indicate, and comparisons with the results of the vapor phase decomposition would be meaningless.

The fact that increasing the surface to volume ratio shows no effect upon the products when the flow method is used and the temperature is above 400° indicates either that the reactions are nearly all homogeneous or nearly all wall reactions. If the latter is true, increasing the surface area would have an effect only on the rate of reaction of the free radicals, not on the products formed. Paneth and Herzfeld, from a study of the kinetics of the reaction, have shown that the radicals react mainly on the walls, and that only a small fraction react in the homogeneous gas phase.[12] It is evident therefore that most of the reactions described above are wall reactions with the exception of reaction (4), which occurs mainly in the gas phase.

Summary

The products formed by the thermal decomposition of tetraethyllead have been studied under a wide variety of conditions with the purpose of securing information about the reactions of free ethyl radicals.

Evidence is presented to show that four reactions are involved. First, a reaction occurring when the concentration of ethyl groups is low and that of tetraethyllead molecules high, is the extraction of hydrogen from a tetraethyllead molecule by an ethyl radical. Second, two ethyl radicals combine in a wall reaction or a three-body collision to form butane. Third, two ethyl groups react on the walls to form a molecule of hydrogen and two of ethylene. Fourth, a reaction in which an ethyl group takes a hydrogen atom from another ethyl group, producing a molecule each of ethane and ethylene. This reaction occurs mostly in the gas phase, and occurs to a less extent than the others.

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(12) Paneth and Herzfeld. *Z. Elektrochem.*, 8, 9 (1931).

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Transport Numbers in Mixed Aqueous Solutions of Alkali Chlorides. I. Theoretical Remarks

BY PIERRE VAN RYSSELBERGHE

Introduction

In recent years various authors have reported or discussed results of migration experiments on mixed aqueous solutions of potassium and sodium chlorides.[1-7] The general conclusion one is entitled to draw from these papers is that when the total concentration is not too high the transport numbers of the two metallic ions are in satisfactory agreement with those calculated by applying MacInnes' formula.[3] This shows that only simple ions are present in those solutions and that, at equal concentrations, potassium and sodium chlorides are dissociated to the same extent. In order to test further the validity of these conclusions McBain and Van Rysselberghe carried out migration experiments with mixed solutions of potassium and sodium chloride of high total concentration and high ratio between the concentration of sodium chloride and that of potassium chloride.[8] They interpreted their results on the basis of incomplete dissociation. This interpretation is discussed in the present note. In a subsequent paper experimental results obtained with mixtures of cesium and sodium chlorides, potassium and lithium chlorides, rubidium and sodium chlorides and new results obtained with mixtures of potassium and sodium chlorides will be presented and discussed,

Transport Number of One of the Two Metallic Ions in a Binary Mixture of Alkali Chlorides.—Let us call ACl and BCl the two chlorides, C the total concentration in gram molecules per liter, x the ratio of the concentration of ACl to the total concentration C, Λ_{ACl}, Λ_{BCl}, Λ_{A}, Λ_{B}, $\Lambda_{Cl,A}$, $\Lambda_{Cl,B}$ the equivalent conductivities of the salts and ions at the concentration C, T_{A}, T_{B}, T_{Cl} the transport numbers of the ions in the mixture, T°_{A}, T°_{B}, $T^{\circ}_{Cl,A}$, $T^{\circ}_{Cl,B}$ the transport numbers of the ions in solutions of the pure salts at the concentration C. We have the following relations between these various quantities

$$\Lambda_{A} = \Lambda_{ACl} \times T^{\circ}_{A} \tag{1}$$

$$\Lambda_{B} = \Lambda_{BCl} \times T^{\circ}_{B} \tag{2}$$

$$\Lambda_{Cl,A} = \Lambda_{ACl} \times T^{\circ}_{Cl,A} \tag{3}$$

$$\Lambda_{Cl,B} = \Lambda_{BCl} \times T^{\circ}_{Cl,B} \tag{4}$$

$$T^{\circ}_{A} + T^{\circ}_{Cl,A} = 1 \tag{5}$$

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(1) Braley and Hall, THIS JOURNAL, 42, 1770 (1920).

(2) Schneider and Braley. *ibid.*, 46, 1121 (1923).

(3) MacInnes, *ibid.*, 47, 1922 (1925).

(4) Dewey, *ibid.*, 47, 1927 (1925).

(5) Bjerrum and Ebert, *Det. Kgl. Danske Videnskabernes Selskab.* VI, *9, p.* 5 (1925).

(6) Braley and Rippie, THIS JOURNAL, 49, 1493 (1927).

(7) See also: Taylor, *ibid.*, 48, 599 (1926).

(8) McBain and Van Rysselberghe, *ibid.*. 64, 2336 (1930).

$$T_B^\circ + T_{Cl,B}^\circ = 1 \qquad (6)$$

$$T_A + T_B + T_{Cl} = 1 \qquad (7)$$

If we assume that the degrees of dissociation and the mobilities of the ions of the two salts in the mixture are the same as those in pure solutions of each of the two salts at the same concentration as the total concentration of the mixture, we have for the transport number of the ion A in the mixture

$$T_A = \frac{x\Lambda_A}{x\Lambda_A + (1-x)\Lambda_B + x\Lambda_{Cl,A} + (1-x)\Lambda_{Cl,B}} \qquad (8)$$

Making use of equations (1), (2), (3), (4), (5) and (6) we obtain

$$T_A = \frac{x\Lambda_{ACl}\,T_A^\circ}{x\Lambda_{ACl} + (1-x)\,\Lambda_{BCl}} \qquad (9)$$

We may consider equation (9) as a mathematical expression of the so-called "isohydric principle."

At concentrations not exceeding 0.1 mole per liter the alkali chlorides may be considered as dissociated to the same extent at equal concentrations.[3,9] We have then

$$\Lambda_{Cl,A} = \Lambda_{Cl,B} = \Lambda_{Cl} \qquad (10)$$

or, according to equations (3) and (4)

$$\Lambda_{ACl} \times T_{Cl,A}^\circ = \Lambda_{BCl} \times T_{Cl,B}^\circ \qquad (11)$$

or, according to equations (5) and (6)

$$\Lambda_{Cl} = \Lambda_{ACl} \times (1 - T_A^\circ) = \Lambda_{BCl} \times (1 - T_B^\circ) \qquad (12)$$

The transport number of the ion A in the mixture, given by equation (8), becomes according to equation (10)

$$T_A = \frac{x\Lambda_A}{x\Lambda_A + (1-x)\Lambda_B + \Lambda_{Cl}} \qquad (13)$$

or, according to equation (1), (2) and (12)

$$T_A = \frac{x\Lambda_{ACl}\,T_A^\circ}{x\Lambda_{ACl}\,T_A^\circ + (1-x)\,\Lambda_{ACl}\cdot\dfrac{1-T_A^\circ}{1-T_B^\circ}\cdot T_B^\circ + \Lambda_{ACl}\,(1-T_A^\circ)} \qquad (14)$$

$$T_A = \frac{T_A^\circ\,(1-T_B^\circ)}{T_A^\circ - T_B^\circ + \dfrac{1-T_A^\circ}{x}} \qquad (15)$$

This formula has been established by MacInnes[3] and has been found to agree with certain experimental results of Schneider and Braley,[2] Dewey,' and Braley and Rippie.[6] It must be kept in mind that equation (9) is general as long as the isohydric principle holds and that equation (15) is valid only in the range of concentrations for which relation (12) holds. In the case of potassium and sodium chloride relation (12) holds strictly up to concentrations of about 0.1 gram molecule per liter.

The transport number T_A as given by equation (9) or (15) is, by definition, the number of gram equivalents of A^+ migrated to the cathode when

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(9) MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, 23, 400 (1927).

one faraday of current has passed through the solution. In order to compare the state of dissociation of the salt ACl in the mixture with its state of dissociation when present alone, it is convenient to compare the number of equivalents of A+ migrated to the cathode when one faraday of current has been carried by the salt ACl in the mixture with the transport number of A+ in a solution of ACl alone of the same concentration as the total concentration of the mixture.

If the salts ACl and BCl are dissociated to practically the same extent in solutions of equal concentration, the fraction of the total current carried by ACI can be calculated by means of the isohydric principle. This fraction is

$$\gamma = \frac{x\Lambda_{\mathrm{ACl}}}{x\Lambda_{\mathrm{ACl}} + (1 - x)\,\Lambda_{\mathrm{BCl}}} \tag{16}$$

As expected, dividing T_{A} as given by (9) by y, we obtain

$$T_{\mathrm{A}} \times \frac{1}{\gamma} = T_{\mathrm{A}}^{\circ} \tag{17}$$

If the isohydric principle really holds in these mixed solutions, the experimental value of T_{A} should always obey equation (9) and dividing it by γ one should always find T_{A}° the transport number of A+ in a solution of ACl alone of the same concentration as the total concentration of the mixture.[10] The results of McBain and Van Rysselberghe[S] at the concentrations 2 and 5 N (x = 0.10, 0.04, 0.02) and those of Schneider and Braley[2] at the concentrations 0.8 and 1.6 N (x = 0.75, 0.67, 0.50, 0.33, 0.25) show that at these concentrations the isohydric principle as embodied in equation (9) does not hold.

McBain and Van Rysselberghe[S] developed a qualitative reasoning in which y is calculated by supposing that the salts are independent and the decrease in the transport number of K^+ is considered as due to the change in the degree of dissociation of potassium chloride caused by the addition of *a* large amount of sodium chloride. This reasoning can be summed up by the formula

$$T_{\mathrm{A}} \times \frac{1}{\gamma} = T_{\mathrm{A}}' \times \frac{a}{\alpha'}, \tag{18}$$

in which T_{A}' is the transport number of A+ in a solution of ACl at the concentration xC, a' the degree of dissociation at this same concentration and α the degree of dissociation of ACl in the mixture. It was found that by using degrees of dissociation deduced from the Nernst theory[11,12] of electrolytic dissociation the experimental results could be satisfactorily accounted for.

The problem, however, deserves a more detailed scrutiny. In order to account for the measured values of T_{A} various lines of theoretical reasoning

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(10) McBain and Van Rysselberghe (Ref. 8) use $T_{\mathrm{A}} \times 1/\gamma$ instead of T_{A}.

(11) Nernst, *Z. physik. Chcm.*, 135, 237 (1928).

(12) Orthmann, *Ergebnisse der exakten Naturwissenschaftcn*, *6*, 155 (1927).

might be followed. One might suppose that dissociation is complete at all concentrations and calculate the mobilities according to the Debye–Hückel–Onsager theory.[13] Such an attempt has been made by Bennewitz, Wagner and Küchler.[14] Since the Onsager conductivity theory gives at most the limiting slope of a mobility or conductivity curve and since appreciable departures from equation (9) (at least in the case of alkali chlorides) appear at concentrations where the theory certainly does not hold, such attempts can hardly be considered as significant.

Empirical equations for the variation of transport numbers with concentration have been established by Jones and Dole[15] and by Longsworth.[16] They are useful for interpolation but it is evident that they do not help the solution of our problem.

Since the direct calculation of mobilities in concentrated mixtures is probably theoretically impossible, we shall try to base the interpretation of experimental data upon the following hypothesis: *in any mixture of two alkali chlorides the mobilities of the various ions are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture.* This hypothesis is obviously different from the isohydric principle (see equation 9).

Let us call u_A, u_B, u_{Cl} the mobilities of the three ions in the mixture of total concentration C; $\overset{\circ}{u}_A$, $\overset{\circ}{u}_{Cl,\,A}$, $\overset{\circ}{u}_B$, $\overset{\circ}{u}_{Cl,\,B}$ the mobilities of these ions in solutions of ACl and BCl of concentration C; α and β the degrees of dissociation of ACl and BCl in the mixture. The transport number T_A in the mixture is given by

$$T_A = \frac{\alpha x u_A}{\alpha x\,(u_A + u_{Cl}) + \beta\,(1 - x)\,(u_B + u_{Cl})} \qquad (19)$$

or

$$T_A = \frac{\alpha x \dfrac{u_A}{u_{Cl}}}{\alpha x \left(1 + \dfrac{u_A}{u_{Cl}}\right) + \beta\,(1 - x)\left(1 + \dfrac{u_B}{u_{Cl}}\right)} \qquad (20)$$

According to our hypothesis

$$\frac{u_A}{u_{Cl}} = \frac{\overset{\circ}{u}_A}{\overset{\circ}{u}_{Cl,\,A}} = \frac{\overset{\circ}{T}_A}{\overset{\circ}{T}_{Cl,\,A}} \qquad (21)$$

and

$$\frac{u_B}{u_{Cl}} = \frac{\overset{\circ}{u}_B}{\overset{\circ}{u}_{Cl,\,B}} = \frac{\overset{\circ}{T}_B}{\overset{\circ}{T}_{Cl,\,B}}$$

Hence

$$T_A = \frac{\alpha x \dfrac{\overset{\circ}{T}_A}{\overset{\circ}{T}_{Cl,\,A}}}{\alpha x \left(1 + \dfrac{\overset{\circ}{T}_A}{\overset{\circ}{T}_{Cl,\,A}}\right) + \beta\,(1 - x)\left(1 + \dfrac{\overset{\circ}{T}_B}{\overset{\circ}{T}_{Cl,\,B}}\right)} \qquad (22)$$

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(13) Onsager, *Physik. Z.* **27**, 388 (1926); **28**, 277 (1927).

(14) Bennewitz, Wagner and Küchler, *ibid.*, **30**, 623 (1929).

(15) Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

(16) Longsworth, *ibid.*, **54**, 2741 (1932).

It can easily be shown that if $a = \beta$ this relation reduces to the MacInnes formula (15), as one would naturally expect.

From (22) we deduce

$$\frac{\alpha}{\beta} = \frac{1-x}{x} \frac{T_{\mathrm{A}}}{T^{\circ}_{\mathrm{A}} - T_{\mathrm{A}}} \frac{T^{\circ}_{\mathrm{Cl,A}}}{T^{\circ}_{\mathrm{Cl,B}}} \qquad (23)$$

It can also be shown that T_{A} and T_{B} obey the relation

$$T_{\mathrm{A}} X T_{\mathrm{B}} = (T^{\circ}_{\mathrm{A}} - T_{\mathrm{A}})(T^{\circ}_{\mathrm{B}} - T_{\mathrm{B}}) \qquad (24)$$

which is equivalent to

$$\frac{T_{\mathrm{A}}}{T^{\circ}_{\mathrm{A}}} + \frac{T_{\mathrm{B}}}{T^{\circ}_{\mathrm{B}}} = 1 \qquad (25)$$

This shows that for a given total concentration the points having T_{A} and T_{B} as coordinates lie on a straight line whose intercepts on the axes are T°_{A} and T°_{B}.

This property is of course verified at low concentrations, where the MacInnes formula is found to hold. Even at the concentration 1.6, investigated by Schneider and Braley,[2] relation (24) is approximately verified. In a subsequent paper it will be shown that at still higher concentrations (2, 4 and 5 N) and even when x becomes very small the MacInnes formula (or formula (22) with $a = \beta$) holds rather well, a result indicating that alkali chlorides are probably dissociated to the same extent at all concentrations and in all mixtures.

Let us now examine two other ways of interpreting migration data on mixtures of alkali chlorides.

1. The ***isohydric principle*** as embodied in equation (9) implies that

$$\alpha\,(u_{\mathrm{A}} + u_{\mathrm{Cl}}) = \alpha^{\circ}\,(u^{\circ}_{\mathrm{A}} + u^{\circ}_{\mathrm{Cl,A}}) \qquad (26)$$

and

$$\beta\,(u_{\mathrm{B}} + u_{\mathrm{Cl}}) = \beta^{\circ}\,(u^{\circ}_{\mathrm{B}} + u^{\circ}_{\mathrm{Cl,B}})$$

α° and β° being the degrees of dissociation of ACl and BCl in solutions of concentration C. At low concentrations

$$\alpha^{\circ}\, u^{\circ}_{\mathrm{Cl,A}} = \beta^{\circ}\, u^{\circ}_{\mathrm{Cl,B}} \qquad (27)$$

and supposing that

$$u^{\circ}_{\mathrm{Cl,A}} = u^{\circ}_{\mathrm{Cl},B} \qquad (28)$$

one finds

$$\alpha^{\circ} = \beta^{\circ} \qquad (29)$$

From the fact that at these low concentrations equation (9) is verified one deduces that $a = \beta$.

At high concentrations (larger than 0.1 N) relation (27) does not hold and neither the isohydric principle (26) nor equation (9) can be considered as significant.

2. The ***principle of independency of the two salts in the mixture*** gives

$$T_{\mathrm{A,i}} = \frac{\alpha' x u'_{\mathrm{A}}}{\alpha' x\,(u'_{\mathrm{A}} + u'_{\mathrm{Cl,A}}) + \beta'\,(1-x)\,(u'_{\mathrm{B}} + u_{\mathrm{Cl,B}})} \qquad (30)$$

in which the primes refer to the concentration xC for ACl and to the concentration $(1-x)C$ for BCl. Taking the ratio of T_A as given by *(19)* to $T_{A,i}$ as given by **(30)** we have

$$\frac{T_A}{T_{A,i}} = \frac{\alpha}{\alpha'} \cdot \frac{u_A}{u'_A} \cdot \frac{\alpha' x(u'_A + u'_{Cl,A}) + \beta'(1-x)(u'_B + u'_{Cl,B})}{\alpha x(u_A + u_{Cl}) + \beta(1-x)(u_B + u_{Cl})} \quad (31)$$

When x tends toward zero, this ratio tends toward

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha u_A}{\alpha' u'_A} \quad (32)$$

Dividing both terms of the ratio by u_A^∞, the mobility of A^+ at infinite dilution, we have

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha \dfrac{u_A}{u_A^\infty}}{\alpha' \dfrac{u'_A}{u_A^\infty}} \quad (33)$$

$\alpha(u_A/u_A^\infty)$ might be considered as a *dynamic degree of dissociation.* We have then

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha_d}{\alpha'_d} \quad (34)$$

a relation analogous to equation *(18)* used by McBain and Van Rysselberghe in the case of very small values of x. Their interpretation of the values of T_K in mixtures of potassiuim chloride and sodium chloride suggests the possibility of establishing a set of dissociation constants in terms of the $\alpha'_d s$. It will be shown, however, in subsequent papers that within the limits of experimental error the MacInnes formula, based on our general hypothesis, accounts satisfactorily for most of the experimental data and that any further calculation of degrees of dissociation or dissociation constants is rendered hardly significant on account of the rather small degree of accuracy of the experimental results.

1. If the fraction γ of the current carried by ACl is calculated according to the hypothesis of proportionality of the mobilities to their values in solutions of ACl and BCI alone of the same concentration as the total concentration of the mixture, relation (17) is always satisfied. Hence the transport numbers of the positive ions in the mixture are the same as in solutions of the pure salts of the same concentration as the mixture, when the transport is expressed in terms of one faraday carried by the respective chlorides.

2. It has come to our attention that Guggenheim and Unmack[17] in their studies of cells with liquid junctions propose a hypothesis of the same type as ours. They state it as follows: "...the ratio of the mobility of a given ion in one solution to its mobility in another solution is the same for all ions..."

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(17) Guggenheim and Unmack, *Det. Kgl. Danske Vidcnskabrrncs Selskab, X, 14,* p. 16 (1931).

Summary

1. The following hypothesis is suggested as the basis of the interpretation of transport numbers in mixtures of alkali chlorides: *The mobilities of the various ions are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture.*

2. The MacInnes formula for the transport number of one of the two positive ions in a mixture of alkali chlorides is a direct consequence of the preceding hypothesis. The range of validity of this formula is now unrestricted.

3. Other methods of interpreting transport numbers in mixtures of alkali chlorides are discussed and shown to be probably without significance.

STANFORD UNIVERSITY, CALIFORNIA

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Transport Numbers in Mixed Aqueous Solutions of Alkali Chlorides. II. Transport Numbers of the Potassium, the Rubidium and the Cesium Ions in Concentrated Solutions of Sodium Chloride, and of the Potassium Ion in Concentrated Solutions of Lithium Chloride

BY PIERRE VAN RYSSELBERGHE AND LEE NUTTING

I. Mixtures of Potassium and Sodium Chlorides.—The movement of potassium in the following mixed solutions of potassium and sodium chloride

0.2 molar KCl + 1.8 molar NaCl
0.08 molar KCl + 1.92 molar NaCl
0.5 molar KCl + 4.5 molar NaCl
0.2 molar KCl + 4.8 molar NaCl

was measured by McBain and Van Rysselberghe.[1] The transport numbers were computed according to the isohydric principle and also according to the principle of independency of the two salts in the mixture. The latter set of transport numbers led to an interpretation of the results based upon unequal values of the dissociation constants of the two chlorides as in the Nernst theory of electrolytic dissociation. As shown in the first paper of this series,[2] the MacInnes formula derived from the hypothesis that *the mobilities of the various ions in the mixture are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture* affords a more straightforward interpretation of the experimental results.

Table I gives, for the five mixtures investigated by McBain and Van Rysselberghe: (1) the composition of the mixture; (2) the transport

(1) McBain and Van Rysselberghe, THIS JOURNAL, 52, 2336 (1930).

(2) Van Rysselberghe, *ibid.*, 55, 990 (1933), henceforth called Paper I.

number of the potassium ion calculated according to the MacInnes formula (see paper I, formula (22), in which a and β are equal)

$$T_{\mathrm{A}} = \frac{x\,\dfrac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,\,A}}}}{x\left(1 + \dfrac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,\,A}}}\right) + (1 - x)\left(1 + \dfrac{T^{\circ}_{\mathrm{B}}}{T^{\circ}_{\mathrm{Cl,\,B}}}\right)} \qquad (1)$$

(3) the experimental transport number; (4) the ratio α/β of the degrees of dissociation of potassium and sodium chlorides in the mixture, calculated according to the formula (see Paper I, formula (23))

$$\frac{\alpha}{\beta} = \frac{1 - x}{x} \times \frac{T_{\mathrm{A}}}{T^{\circ}_{\mathrm{A}} - T_{\mathrm{A}}} \times \frac{T^{\circ}_{\mathrm{Cl,\,A}}}{T^{\circ}_{\mathrm{Cl,\,B}}} \qquad (2)$$

The numerical values of the transport numbers T°_{K}, T°_{Na}, etc., were taken from the Landolt–Börnstein–Roth tables and from the recent paper of MacInnes and Dole.[3]

TABLE I

Concentration of mixture, moles per liter	T_{K} MacInnes	T_{K} Measured	α/β
0.2 KCl + 1.8 NaCl	0.060	0.057	0.96
0.08 KCl + 1.92 NaCl	.024	.019	.78
0.04 KCl + 1.96 NaCl	.012	.010	.82
0.5 KCl + 4.5 NaCl	.061	.052	.84
0.2 KCl + 4.8 NaCl	.025	.025	1.00

McBain and Van Rysselberghe[4] expressed the values of T_{K} in terms of one faraday of current carried by potassium chloride. In Table I, T_{K} is expressed in terms of one faraday carried by the mixture. By examining Table III of McBain and Van Rysselberghe's paper, one will notice that the discrepancy between the two sets of values of T_{K} reported in Table I is of the same order as the experimental error. It might seem that the fact that most of the experimental values of T_{K} are smaller than the calculated ones indicates a systematic discrepancy. This is certainly not the case as the new data obtained with a total concentration of 4 *N* exhibit a departure in the other direction from the values calculated by means of the MacInnes formula.

These data are reported in Table II. They were obtained by exactly the same method as those of McBain and Van Rysselberghe.[1]

Apparatus.—Three U-tubes with ground joints, three middle portions; precipitation of potassium as potassium sodium cobaltinitrite; temperature, ±25°; current strength, +40 milliamperes; length of each run, four to four and one-half hours.

In Table III the experimental values of T_{K} are compared with those deduced from the MacInnes formula and the values of α/β calculated according to formula (2) are given.

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(3) MacInnes and Dole. THIS JOURNAL, 53, 13.57 (1931)

(4) Ref. 1, p. 2341.

TABLE II

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND SODIUM CHLORIDES. TOTAL CONCENTRATION 4 N

Concn. of mixture, moles per liter	Ratio $\frac{\text{NaCl}}{\text{KCl}}$	Ag in coulometer, g.	Change in K content Middle, %	Anode, mg.	Cathode, mg.	T_K
0.2 KCl + 3.8 NaCl	19	0.6809	0.6	−11.7	+7.0	0.038
				−7.7	+11.3	
0.1 KCl + 3.9 NaCl	39	.8385	0.6	−3.5	+6.5	.018
				−3.8	+4.9	
				−5.7	+8.4	
0.1 KCl + 3.9 NaCl	39	.6717	1.3	−3.9	+2.8	.015
				−4.4	+3.7	

TABLE III

Concn. of mixture, moles per liter	T_K MacInnes	T_K measured	α/β
0.3 KCl + 3.8 NaCl	0.030	0.038	1.05
0.1 KCl + 3.9 NaCl	.015	.016 (av.)	0.98

Considering together the data of Table I and of Table III and noting that the values of α/β are probably accurate to ±0.2, it seems that the MacInnes formula holds for these mixtures and that the two chlorides are dissociated to the same extent, within the limits of experimental error. The average value of α/β for the seven mixtures is 0.92.

2. Mixtures of Rubidium and Sodium Chlorides.—The movement of the rubidium ion was measured in various mixtures of rubidium and sodium chloride of total concentration 2 and 4 N, the ratio between the total concentration and that of rubidium chloride being 20 and 40.

The experimental method was the same as that of McBain and Van Rysselberghe. The rubidium chloride used was obtained from C. P. Kahlbaum rubidium iodide which was treated with an excess of chlorine. The iodine was evaporated off, the rubidium chloride was purified by several successive recrystallizations and thoroughly dried. C. P. General Chemicals sodium chloride was used. Rubidium was precipitated as rubidium chloroplatinate. On account of the small solubility of sodium chloride in alcohol the usual procedure had to be slightly modified. The samples were treated by the same excess of 10% solution of C. P. General Chemicals chloroplatinic acid and the precipitates were allowed to settle for at least twelve hours. The liquid was then decanted on weighed filters. Alcohol was added to the residues and filtration was carried out. The precipitates were washed several times with alcohol. The filters were dried at 120° and weighed. Nine weighed samples of about 10 cc. were analyzed for each experiment, namely, two samples of the original solution, two of the cathode portion, two of the anode portion, one of each, the central, anode and cathode middle portions: temperature, ±25°; current strength, *40 milliamperes; length of each run, four to four and one-half hours. The results are given in Table IV.

TABLE IV

MIGRATION DATA FOR MIXTURES OF RUBIDIUM AND SODIUM CHLORIDES

Concn. of mixture. moles per liter	Ratio $\frac{NaCl}{RbCl}$	Ag in coulometer, g.	Change in Rb content Middle, %	Anode, mg.	Cathode, mg.	T_{Rb}
0.1 RbCl + 1.9 NaCl	19	0.7408	0.1	−20.0 −20.8	...	0.035
0.1 RbCl + 1.9 NaCl	19	.6689	1.2	−23.9 −19.2	+11.7 +15.2	.033
0.05 RbCl + 1.95 NaCl	39	.6469	0.2	− 9.9 9.2	f9.1 + 6.1	.017
0.2 RbCl + 3.8 NaCl	19	.8320	1 0	--RO.l −20.5	+12.0 +18.1	.031
0.1 RbCl + 3.9 NaCl	39	.8257	1.1	−10.8 − 6.0	+10.7 +10.8	.015

In Table V the experimental values of T_{Rb} are compared with those deduced from the MacInnes formula and the values of α/β calculated according to formula (2) are given. The values of T°_{Rb} were taken equal to those of T°_{K} at the same concentrations.

TABLE V

Concn. of mixture, moles per liter	T_{Rb} MacInnes	T_{Rb} measured	α/β
0.1 RbCl + 1.9 NaCl	0.030	0.034	1.18
0.05 RbCl + 1.95 NaCl	.015	.017	1.13
0.2 RbCl + 3.8 NaCl	.030	.031	1.05
0.1 RbCl + 3.9 NaCl	.015	.015	1.00

One sees again that the two sets of transport numbers agree within the limits of experimental error. If, moreover, one notes that there is a certain element of uncertainty in the values of T°_{Rb}, it seems safe to conclude that the probable value of α/β is unity. The average α/β for the four mixtures is 1.09.

3. Mixtures of Cesium and Sodium Chlorides.—The movement of the cesium ion was measured in four mixtures of cesium and sodium chlorides analogous to the four mixtures of rubidium and sodium chlorides of the foregoing section of this paper. The method was identical with the one described in this section. C. P. Kahlbaum cesium chloride and C. P. General Chemicals sodium chloride were used.

The experimental results are reported in Table VI. In Table VII the experimental values of T_{Cs} are compared with those deduced from the MacInnes formula and the values of α/β calculated according to formula (2) are given. The values of T°_{Cs} were taken equal to those of T°_{K} at the same concentrations.

The values of α/β are rather smaller than 1. If this is significant it might simply mean that T°_{Cs} is smaller than T°_{K} at these high concentrations, but since for all the mixtures investigated here α/β is probably ac-

TABLE VI

MIGRATION DATA FOR MIXTURES OF CESIUM AND SODIUM CHLORIDES

Concn. of mixture, moles per liter	Ratio NaCl/CsCl	Ag in coulometer, g.	Change in Cs content			T_{Cs}
			Middle, %	Anode, mg.	Cathode, mg.	
0.1 CsCl + 1.9 NaCl	19	0.7464	0.2	−23.5	$24.8	0.026
				−22.7	+24.0	
0.05 CsCl + 1.95 NaCl	39	1.1270	.2	+19.2	−19.0	.014
				+19.1	−19.0	
0.2 CsCl + 3.8 NaCl	19	1.1536	.2	+40.6	−32.8	.026
				+40.7	...	
0.1 CsCl + 3.9 NaCl	39	1.0385	.2	+12.6	−21.2	.013
				+16.8	−15 2	

TABLE VII

Concn. oi mixture, moles per liter	T_{Cs} MacInnes	T_{Cs} measured	α/β
0.1 CsCl + 1.9 NaCl	0.030	0.026	0.86
0.05 CsCl + 1.95 NaCl	.015	.014	.92
0.2 CsCl + 3.8 NaCl	.030	.026	.85
0.1 CsCl + 3.9 NaCl	.015	,013	.84

curate to only ±0.2, it seems that cesium and sodium chlorides are dissociated to the same extent, within the limits of experimental error.

The average value of α/β for the four mixtures is 0.87 and the average α/β for all the mixtures studied so far is 0.95.

4. Mixtures of Potassium **and** Lithium **Chlorides.**—The movement of the potassium ion in mixed aqueous solutions of potassium and lithium chlorides of total concentration *2* and 4 *N*, the ratio between the total concentration and that of potassium chloride being 20 and 40, was measured. The experimental method was the same as that used for the other mixtures studied in this paper. C. P. Kahlbaum lithium chloride and C. P. General Chemicals potassium chloride were used. Potassium was precipitated and weighed as potassium sodium cobaltinitrite, according to the method previously used for the mixtures of potassium and sodium chlorides.[5,1] The accuracy of the analyses was of the order of 1%.

The results are reported in Table VIII.

In Table IX the measured transport numbers are compared with those calculated by means of the MacInnes formula and the values of α/β calculated by means of formula (2) are given. The values of T°_{Li} were taken from the Landolt–Bornstein–Roth tables.

The agreement between the measured and the calculated values of T_K is again within the limits of experimental error. The departure from 1 of the ratio α/β is probably not significant.

The average α/β for these four mixtures is 1.08.

The average α/β for all the mixtures studied in this paper is 0.99.

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(6) Van Rysselberghe, *Ind.* Eng. *Chem.*, *Anal. Ed.*, 3, 3 (1931)

TABLE VIII

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND LITHIUM CHLORIDES

Concn. of mixture, moles per liter	Ratio $\frac{\text{LiCl}}{\text{KCl}}$	Ag in coulometer, g.	Change in K content Middle. %	Anode, mg.	Cathode, mg.	T_K
0.1 KCl + 1.9 LiCl	19	0.5805	0.3	−8.0	+7.2	0.037
				−9.1	+6.7	
0.1 KCl + 1.9 LiCl	19	.6905	1.7	−8.2	+10.3	.036
				−8.2	+8.9	
0.05 KCl + 1.95 LiCl	39	.7515	0.2	−4.9	+4.1	.019
				−5.8	+4.8	
				−6.2	+6.2	
0.2 KCl + 3.8 LiCl	19	.6678	0.5	−9.3	+6.6	.036
				−9.0	+10.0	
0.1 KCl + 3.9 LiCl	39	.6522	0.1	−5.8	+2.9	.022
				...	+6.5	
				−4.9	+5.3	

TABLE IX

Concn. of mixture, moles per liter	T_K MacInnes	T_K measured	α/β
0.1 KCl + 1.9 LiCl	0.034	0.036	1.05
0.05 KCl + 1.95 LiCl	.017	.019	1.09
0.2 KCl + 3.8 LiCl	.034	.036	1.07
0.1 KCl + 3.9 LiCl	,017	.022	1.11

Summary

1. The MacInnes formula for the transport number of one of the two metallic ions in a mixture of alkali chlorides, as derived from the fundamental hypothesis developed in Paper I of this series, accounts for the transport numbers of the potassium, the rubidium and the cesium ions in mixtures of their chlorides with large amounts of sodium chloride and for the transport numbers of the potassium ion in mixtures of its chloride with large amounts of lithium chloride

2. It seems then likely that, within the limits of experimental error: (A) the mobilities of the various ions in these mixtures are proportional to their values in solutions of the chlorides alone of the same concentration as the total concentration of the mixture; (B) the alkali chlorides are dissociated to the same extent in all the mixtures investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF CINCINNATI]

The Crystal Structure of Precipitated Copper–Tin Alloys

BY H. KERSTEN AND JOSEPH MAAS

It has been shown by Mylius and Fromm[1] that tin added to a neutral or slightly acid 1% aqueous solution of copper sulfate produces a precipitate whose composition approximately agrees with that of Cu_3Sn. It was the purpose of this investigation to determine whether the crystal structure of the precipitated alloy is the same as that of a fused alloy of like composition. During the investigation it was found that the composition of the alloy could be varied from nearly pure copper to nearly 40% tin by changing the amount of acid in the solution. These percentages include the a-phase as well as the one containing Cu_3Sn, so that the structure of the precipitated α-bronze was also compared with that of fused a-bronze.

The crystal structures of fused Cu_3Sn and a-bronze have been carefully investigated by Jones and Evans,[2] Weiss[3] and Westgren and Phragmén,[4] so that it was unnecessary to prepared fused alloys for comparison.

Experimental

The x-rays were supplied by a gas tube[5] having a copper target and equipped with a reflection spectrograph.[6] The tube was operated at about *25* kv. and **30** ma.

The samples were prepared by adding 5 g. of lead-free tin foil to beakers of hot (80°) 1% aqueous solutions of $CuSO_4 \cdot 5H_2O$ containing various quantities of sulfuric acid. These were kept at SO° for five hours and then allowed to cool gradually to room temperature. It was found that the same alloys could be produced with smaller quantities of tin foil as well as at other temperatures, but that at the lower temperatures a longer time was required for the alloys to form, especially in the case of the less acid solutions. During the time the alloys were being precipitated, the solutions were stirred occasionally. After the solutions had cooled to room temperature, the liquid was decanted and the precipitate washed several times to get rid of a white sediment which had formed, and which tended to remain suspended in the liquid more easily than the alloy. The precipitate was dried at 120° and cooled in a desiccator before the chemical and crystal structure analyses were made.

Results

The percentages of tin and copper in the precipitated alloys are plotted

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(1) Mylius and Fromm, *Ber.*, 27,630 (1894).

(2) Jones and Evans, *Phil. Mag.*, [7] 4, 1302 (1927).

(3) Weiss *Proc. Roy. Soc.* (London). A108, 643 (1925).

(4) Westgren and Phragmén, Z. *anorg. allgem. Chem.*, 175, 80 (1928).

(5) Kersten, *Rev. Sci. Inst.*, 8, 145 (1923).

(6) Kersten, *ibid.*, 8, 384 (1923).

as functions of the number of cc. of concentrated sulfuric acid per liter of solution in Fig. 1.

The curves show that there is a preferred tendency to precipitate either α-bronze or Cu_3Sn. All the precipitated alloys contained sulfur in addition to tin and copper. This probably makes up the difference between 100% and the total per cent. of metal.

In column 3 of Table I are given all the observed values of 2Θ for precipitated Cu_3Sn Column 2 gives the corresponding a-lines observed by Jones and Evans[2] for fused Cu_3Sn, as well as values for several β-lines. The β-lines were computed from the theoretical spacings given by the authors just mentioned.

Table II shows a similar comparison of the lines of precipitated α-bronze with those computed, assuming a face-centered cube whose side is equal to 3.623 Å. as given by Weiss.[3]

No lines, other than those listed, were observed. For each phase the agreement is sufficiently close to show that precipitated a-bronze and precipitated Cu_3Sn have the same structure as the corresponding alloys prepared by fusion.

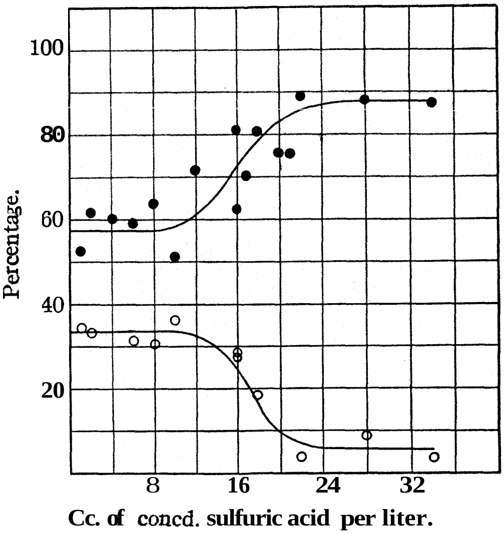

Fig. 1.—Percentages of tin and copper in the precipitated alloys as a function of the number of cc. of sulfuric acid per liter: upper curve, copper; lower curve, tin.

TABLE I

1 Planes	2 Lines for fused Cu_3Sn	3 Lines for precipitated Cu_3Sn
. .	. . . . .	30° 50′
100β	33° 54′	35°
100α	37° 44′	39°
101β	38° 56′	39° 50′
101α	43° 28′	44°
102β	51° 2′	52°
. .	. . . . .	63° 40′
102α	57° 34′	58° 20′
110α	68° 2′	69°
201α	84° 28′	84°
203α	114° 24′	114° 40′
210α	117° 52′	117° 50′
211α	122° 16′	122°
114α	130° 56′	131° 10′

TABLE II

Planes	Computed 2θ	Observed 2θ
111β	38° 42′	38° 50′
111α	43° 12′	43° 30′
200α	50° 18′	50°
220α	73° 52′	74°
311α	89° 40′	89° 50′
222α	94° 48′	94° 40′
331α	135° 40′	136° 10′
420α	144°	144° 10′

Summary

Tin added to a dilute, aqueous, hot, 1% solution of $CuSO_4{:}5H_2O$ containing less than 12 cc. of concentrated sulfuric acid per liter precipitates an alloy corresponding in composition and crystal structure to that of the Cu_3Sn phase prepared by fusion. When the solution contains more than 20 cc. of concentrated sulfuric acid per liter, an alloy corresponding in composition and crystal structure to that of the a-phase of the copper–tin system is precipitated.

CINCINNATI, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Heat of Dilution and the Partial Molal Heat Capacity of Zinc Sulfate from the Electromotive Force of Galvanic Cells

VICTOR K. LA MER AND IRVING A. COWPERTHWAITE[1]

I. Introduction

Although the use of the Gibbs–Helmholtz equation has been recognized for many years as a reliable procedure for calculating changes in heat content in chemical processes from the e. m. f. measurements of galvanic cells, the applications have been restricted almost exclusively to processes involving displacement reactions between metals and their salts.

In spite of the renewed interest in the theoretical interpretation of the caloric properties of electrolytes in the region of high dilution, little use has been made of the method for the determination of heats of dilution of electrolytes in this important region.[2]

The paucity of galvanic cells which will yield reversible e. m. f.'s at the low concentrations necessary for an unambiguous extrapolation to infinite dilution is undoubtedly one reason for the neglect of the method. Skepticism of the reliability of methods involving differentiation for their numerical solution is another. The latter objection, however, is not peculiar to the e. m. f. method, for in the calorimetric method it is necessary to differentiate the measured integral heat of dilution in respect to concentration to calculate the partial molal quantity which is obtained in the e. m. f. method by differentiating the e. m. f. values with respect to temperature.

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(1) This is a second paper constructed from a dissertation submitted in December, 1930, by Irving A. Cowperthwaite to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This paper was presented at the Buffalo (1931) meeting of the Soctety The first paper appeared in THIS JOURNAL, 53,4333 (1931).

(2) Recently Harned and Nims [THIS JOURNAL, 54, 423 (1932)] have computed the partial molal heat of dilution and partial molal heat capacity of sodium chloride solution from 0.05 m to 4 m against the reference state of the 0 1 *m* solution from e. m. f. measurements through the temperature range of 0–40°. See also Harned and Murphy, ibid., 53, 8 (1931); Lewis and Randall. "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc, New York, 1923, p. 392, Ellis, THIS JOURNAL, 38, 737 (1916).

In the previous paper[3] it was shown that the e. m. f. of the cell

$$\text{Zn-Hg (two phase)} \mid ZnSO_4\,(m),\ PbSO_4\,(s) \mid \text{Pb-Hg (two phase)} \qquad (1)$$

corresponding to the process

$$Zn\,(s) + PbSO_4\,(s) = ZnSO_4\,(m) + Pb\,(s) \qquad (2)$$

could be measured with a precision of ±0.05 mv. to concentrations as low as 0.0005 *m* at temperatures of 0, 12.5, 25, 37.5 and 50°. This cell is consequently well suited for our purpose.

The essential improvement which we offer in the use of this method of computing heat quantities consists in the application of the theoretical equations of Gronwall, La Mer and Sandved[4] as a more legitimate means of extrapolating the e. m. f. data to infinite dilution for an exact evaluation of E° as compared to the customary graphical methods. The accurate values of E° thus obtained permit the computation of $\overline{L}_2$ (the relative partial molal heat content) and $\bar{c}_p - \bar{c}_p^\circ$ (the relative partial molal heat capacity) for the solute. The reference state for each of these properties is infinite dilution. The variation of these properties with concentration is the result of interionic attraction.

Inasmuch as the subsequent differentiation process for determining the temperature coefficients of the e. m. f. will exaggerate any experimental error in the individual measurements, we have eliminated these variations as far as possible by employing smoothed values of $E^{\circ\prime}$ (see Eq. 3) computed on the basis of the theoretical equations using the best values of E° and the parameter "*a*" as determined from the original data.[3] This procedure does not eliminate the experimental error in any given measurement, but distributes it more equitably over the entire concentration range rather than focusing it upon one particular concentration. Consequently this method is superior to the customary graphical smoothing since all the experimental data are involved uniformly in the smoothing process.

TABLE I

SMOOTHED VALUES OF $E^{\circ\prime}$

m	0°	12.5°	25°	37.5°	50°
0	**0.43594**	**0.42407**	**0.41086**	**0.39628**	**0.38192**
.0005	.44149	.43001	.41724	.40320	.38924
.001	.44386	.43256	.41999	.40620	.39238
.002	.44704	.43596	.42365	.41018	.39653
.005	.45247	.44176	.42984	.41690	.40349
.01	.45731	.44690	.43531	.42276	.40953

II. Theoretical

In Table I

$$E^{\circ\prime} = E + \frac{\nu}{n}\frac{RT}{F}\ln m \qquad (3)$$

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[3] Cowperthwaite and La Mer, THIS JOURNAL, 53, 4333 (1931).

[4] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

where E is the measured e. m. f. at the molality m. From the expression

$$E = E^\circ - \frac{\nu}{n}\frac{RT}{F}\ln m - \frac{\nu}{n}\frac{RT}{F}\ln f \tag{4}$$

where f is the activity coefficient of the salt at molality m, and E° is a constant

$$E^{\circ\prime} = E^\circ - \frac{\nu}{n}\frac{RT}{F}\ln f\text{[6]} \tag{5}$$

Substituting for E its equivalent $E^{\circ\prime} - \nu RT/nF \ln m$ as defined in equation (3) in the Gibbs–Helmholtz equation

$$-\Delta H = nF\left(E - T\frac{\partial E}{\partial T}\right) \tag{6}$$

and collecting terms

$$-\Delta H = nF\left(E^{\circ\prime} - T\frac{\partial E^{\circ\prime}}{\partial T}\right) \tag{7}$$

Equation (7) is amenable to numerical treatment since $E^{\circ\prime}$ extrapolates to a finite value (E°) whereas E in equation (6) becomes infinite when $m = 0$.

Substituting numerical values for $E^{\circ\prime}$ and $dE^{\circ\prime}/dt$ determined for a given molality m and temperature T in equation (7) yields $-\Delta H$ the decrease in heat content corresponding to the cell process

Zn(solid, saturated with Hg) + $PbSO_4$(s) =
$ZnSO_4$(m) + Pb(solid, saturated with Hg) (8)

Whereas substitution of the values of E° [$= E^{\circ\prime}$ $(m = 0)$] and dE°/dt yield $-\Delta H(m = 0)$, the corresponding thermal quantity for the process (9) when the molality of zinc sulfate is zero.

Zn(solid, saturated with Hg) + $PbSO_4$(s) =
$ZnSO_4$(m = 0) + Pb(solid, saturated with Hg) (9)

If we subtract equation (8) from equation (9), the solids cancel and the heat effect $\bar{L}_2$ corresponding to the transfer of one mole of zinc sulfate from molality (*m*) to infinite dilution remains

$$ZnSO_4(m) = ZnSO_4(m = 0) \tag{10}$$

$\bar{L}_2$, the relative partial molal heat content of aqueous zinc sulfate is defined by

$$-\Delta H\ (\text{Equation } 10) = \bar{H}_2 - \bar{H}^\circ_2 = \bar{L}_2 \tag{11}$$

By subtracting the Gibbs–Helmholtz equation corresponding to process (8) from that corresponding to process (9)

$$\bar{L}_2 = nF\left[(E^\circ - E^{\circ\prime}) - T\left(\frac{\partial(E^\circ - E^{\circ\prime})}{\partial T}\right)\right] \tag{12}$$

Substituting the value of $E^\circ - E^{\circ\prime}$ from equation (5)

$$\bar{L}_2 = nF\left[\frac{\nu}{n}\frac{RT}{F}\ln f - T\left(\frac{\partial\left(\frac{\nu}{n}\frac{RT}{F}\ln f\right)}{\partial T}\right)\right] \tag{13}$$

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(6) In the special case of a bi-bivalent electrolyte, like zinc sulfate to which this paper is restricted, $\nu = 2$ (the number of ions per mole of salt) and $n = 2$ (the number of Faradays involved in the cell process) so that the factor ν/n equals unity. The symbol f will always refer to $f_\pm$ the geometric mean activity coefficient of the salt, and similarly $m = m_\pm$.

Performing the indicated differentiation and collecting terms, the expression[6] for $\bar{L}_2$ can be written.

$$\bar{L}_2 = -\nu RT^2 \frac{\partial \ln f}{\partial T} \tag{14}$$

The limiting law for $\bar{L}_2$ follows by substituting in (14) the expression for $\ln f$ given by the limiting form of the Debye–Hückel theory[7]

$$\bar{L}_2 = \nu RT^2 \frac{\partial}{\partial T}\left(\frac{\epsilon^2 z^2}{kTDa}\cdot\frac{1}{2}\cdot x\right) \tag{15}$$

On carrying out the indicated differentiation, the following expression results[8]

$$\bar{L}_2 = -\frac{3}{4}\nu\frac{R\epsilon^2 z^2}{kD}\kappa\left(1 + \frac{T}{D}\frac{dD}{dT} + \frac{1}{3}\frac{T}{V}\frac{dV}{dT}\right) \tag{16}$$

For a bi-bivalent electrolyte where $\nu = 2$

$$\bar{L}_2 = 5735\sqrt{c} \text{ at } 25° \text{ for } c \longrightarrow 0 \tag{17}$$

$$\bar{L}_2 = 4620\sqrt{c} \text{ at } 12.5' \text{ for } c \longrightarrow 0 \tag{18}$$

Substituting equation (7) in Kirchhoff's formula

$$\Delta C_p = \frac{\partial \Delta H}{\partial T} \tag{19}$$

and simplifying

$$\Delta C_p = nFT\left(\frac{\partial^2 E^{\circ\prime}}{\partial T^2}\right) \tag{20}$$

By subtracting the change in heat capacity for the cell process at infinite dilution from that at molality m, we obtain the change in partial molal heat capacity of the zinc sulfate between molality m and m = 0. By means of the same type of transformations used in deriving (12) and (14)

$$\bar{C}_p - \bar{C}_p{}^{\circ} = nFT\frac{\partial^2}{\partial T^2}(E^{\circ\prime} - E^{0}) \tag{21}$$

$$\bar{C}_p - \bar{C}_p{}^{\circ} = -\frac{\partial}{\partial T}\left[\nu RT^2\frac{\partial}{\partial T}(\ln f)\right] \tag{22}$$

By introducing the Debye–Hückel limiting law for $\ln f$ and performing the differentiations, we get equation **(23)**

$$\bar{C}_p - \bar{C}_p{}^{\circ} = -\frac{3}{8}\frac{\nu R\epsilon^2 z^2}{kTD}\kappa f(DTV) \tag{23}$$

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(6) **Brönsted**, *Z. physik.* Chem., **100, 139 (1922).**

(7) In equation **(15)** R is the gas constant and is equal to **1.9885 cal.** per degree; **T** is the absolute temperature, $\epsilon = 4.774 \times 10^{-10}$ is the charge on the electron; $z = z_1 = -z_2$ is the valence of the ions, which are equal in the case of a symmetrical valence type electrolyte such as zinc sulfate; $k = 1.372 \times 10^{-16}$ is the **Boltzmann** constant; **D** is the dielectric constant of the medium $= 78.54\,[1 - 0.00460\,(t - 25) + 0.0000088\,(t - 25)^2]$ for water according to Wyman [Phys. Rev., **36,623 (1930)**]; '**a**' is the ion size parameter of **Debye** and **Hückel**; $x = \kappa a$ where $\kappa^2 = -4\pi N\epsilon^2\nu z_1 z_2 n/1000kTDV$; N is Avogadro's number $= 6.061 \times 10^{23}$; and **a** is the number of moles of electrolyte in V liters of solution.

(8) **Bjerrum** [*Z. physik. Chem.*, **119, 145 (1926))** derived equation **(16)**, but neglected **the** term containing dV/dT. Scatchard [THIS JOURNAL, **53, 2037 (1931)**] pointed out that this omission introduces an error of +7.2% in the case of water at 25°. The effect of thermal expansion is much less at lower temperatures, being only **1%** at **12 5°**. We use the following values for $TdV/3VdT$, **0 0256** at 25° and **0.0036** at 12.5°.

where

$$f(DTV) = 1 + 2\frac{T}{D}\frac{dT}{dD} + 5\left(\frac{T}{D}\frac{dD}{dT}\right) + 2\frac{T^2}{DV}\frac{dD}{dT}\frac{dV}{dT} + \frac{2}{3}\frac{T}{V}\frac{dV}{dT} + \left(\frac{T}{V}\frac{dV}{dT}\right) - 2\frac{T^2}{D}\frac{d^2D}{dT^2} - \frac{2}{3}\frac{T^2}{V}\frac{d^2V}{dT^2} \qquad (24)$$

Randall and Rossini[9] derived an equation similar to (23) for the limiting slope of $\bar{c}_p-\bar{c}_p{}^\circ$ against $\sqrt{c}$. They, however, neglected the change of volume with temperature. Their equation contains an $f(DT)$ which is equal to our $f(DTV)$ after dropping all terms containing V and its derivatives. The value of $f(DTV)$ is 16% lower than the value of $f(DT)$ at 25°, so the effect of thermal expansion of the solution is even more important in the case of the heat capacity than in the case of the heat of dilution. For a 2–2 electrolyte at 25°, we obtain the following limiting expression valid for $C \longrightarrow 0$

$$\bar{c}_p - \bar{c}_p{}^\circ = 106\sqrt{c} \text{ at } 25^\circ \qquad (25)$$

III. Computations

To evaluate these derivatives in equations (7) and (20), the smoothed values of $E^{\circ\prime}$ were expressed as fourth degree functions of the temperature.[10] The equations are of the form $10^5E^{\circ\prime} = A + BW + CW^2 + DW^3 + EW^4$ where $W = (t-25)/12.5$. The numerical values of the coefficients are given in Table II.

TABLE II

m	A	B	C	D	E
0	41086	−1402.5	−75.25	13.00	6.75
.0005	41724	−1351.9	−6904	11.42	5 54
.001	41999	−1328.3	−65.75	10.33	4.75
.002	42365	−1297.8	−61.79	8.75	3.79
.005	42984	−1249.2	−52.50	6.17	1.50
.01	43531	−1211.2	−48.25	4.17	0.25

By use of these coefficients, the first derivatives are easily evaluated. $\bar{L}_2$ was computed only for the temperatures of 12.5 and 25° where the empirical formulas and the experimental measurements are most reliable for purposes of differentiation. For the same reason the second derivative and $\bar{c}_p-\bar{c}_p{}^\circ$ are calculated only at 25°. Our values of $-$ AH, $\bar{L}_2$, ΔC_p and $\bar{c}_p-\bar{c}_p{}^\circ$ are summarized in Table III.

Equation (20) yields ΔC_p for the process, which is equal to $\bar{c}_p$ ($ZnSO_4,m$) + C_p (Pb) $-$ C_p (Zn) $-$ C_p ($PbSO_4$). Using the value for E^0, we can compute $\bar{c}_p{}^\circ$ for zinc sulfate when the heat capacities of the solids are known. From the "International Critical Tables" (Vol. V, p. 92) ΣC_p (solids) = −25.3 cal. per degree, whence

$$\bar{c}_p{}^\circ(ZnSO_4) = -132.4 - (-25.3) = -107.1 \text{ cal./degree/mole}$$

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(9) Randall and Rossini, THIS JOURNAL, 51, 323 (1929).

(10) The Newton–Stirling central difference interpolation formula is a convenient method for obtaining these equations in a form symmetrical to 25°. *See* Whittaker and Robinson, "The Calculus of Observations," Blackie and Son, Ltd , 1924, equation A, p. 38.

TABLE III

SUMMARY OF COMPUTATIONS

F = 23063 cal./equivalent

m	$E^{\circ\prime}$	$10^3 \frac{dE^{\circ\prime}}{dT}$	$-\Delta H$	$\bar{L}_2$	$10^5 \frac{d^2E^{\circ\prime}}{dT^2}$	ΔC_p	$\bar{c}_p - \bar{c}_p^{\circ}$
			25°				
0	0.41086	−1.1220	34380	000	−0.9632	−132.4	0
.0005	.41724	−1.0815	34114	266	− .8840	−121.6	10.8
.001	.41999	−1.0627	33985	395	− .8416	−115.7	16.7
.002	.42365	−1.0382	33817	563	− .7909	−108.8	23.7
.005	.42984	−0.9993	33568	812	− .6720	− 92.4	40.0
.01	.43531	−0.9689	33402	978	− .6176	− 84.9	47.5
			12.5°				
0	0.42407	−0.9920	32630	000			
.0005	.43001	− .9612	32498	132			
.001	.43256	− .9479	32440	190			
.002	.43596	− .9305	32368	262			
.005	.44176	− .9053	32303	327			
.01	.44690	− .8825	32240	390			

In the absence of data on the heat capacity of zinc and lead both saturated with mercury we have employed values for the pure metals. The uncertainty in all probability is negligible for zinc but merits further investigation in the case of lead.

The calorimetric method of determining heats of dilution gives L = $n_1\bar{L}_1 + n_2\bar{L}_2$, the integral heat of dilution. In order to compare our results with those obtained in the calorimetric method, we have computed L by integrating graphically, using the formula $L = \int_0^{n_2} \bar{L}_2 dn_2$. The results are given in Table IV.

TABLE IV

THE INTEGRAL HEAT OF DILUTION OF ZINC SULFATE AT 25°

m	0.0005	0.001	0.002	0.005	0.01
L	157	246	366	571	739

PV. Discussion of Results

The values of $\bar{L}_2$ and $\bar{c}_p - \bar{c}_p^{\circ}$ are plotted against the $\sqrt{m}$ in Figs. 1 and 2. It is evident that $\bar{L}_2$ and $\bar{c}_p - \bar{c}_p^{\circ}$ are far from being linear functions of the square root of m even at concentrations as low as 0.0005 m. The figures emphasize what misleading results can be obtained by extrapolating linearly calorimetric data for high valence type electrolytes from concentrations as low as 0.01 m to zero concentration by means of the Debye–Huckel limiting slope.[11]

Randall and Rossini,[9] who first derived equation (23), employed E. Q. Adams' exponential representation of Kockel's data for D and computed

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(11) In a later paper we shall publish our development of the function for $\bar{L}_2$ on the basis of the Gronwall, La Mer and Sandved[4] extension of the Debye–Huckel theory and compare our results with this more complete expression.

$f(DT) = 1.75$, corresponding to a limiting slope for the partial molal heat capacity for a (2,–2) salt against $\sqrt{m}$ equal to 48 in place of our value of 106.

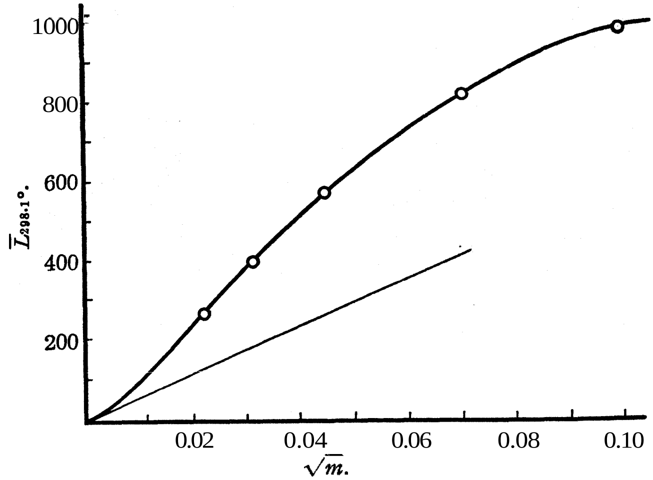

Fig. 1.—The partial molal heat content $\bar{L}_2$ of aqueous solutions of zinc sulfate at 298.1°K. in calories per mole. The straight line represents the limiting law of the Debye–Hückel theory.

For the (1,–1) and (1,–2) salts, which they measured down to $m = 0.04$, they noted that the approximate limiting slopes of $\bar{C}_p - \bar{C}_p^{\circ}$ against $\sqrt{m}$ were 2 to 3 times that calculated by their formula, a difficulty which is now largely removed by the use of the Wyman formula, which yields

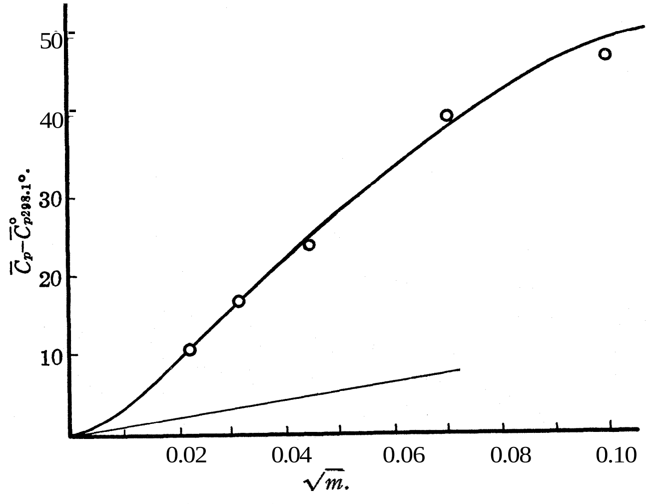

Fig. 2.—The influence of concentration upon the partial molal heat capacity of zinc sulfate in aqueous solution. The straight line represents the Debye–Hückel limiting law.

$f(DT) = 4.535$ and $f(DTV) = 3.802$. The computation of $\partial^2E^{\circ\prime}/\partial T^2$ is so sensitive to experimental errors in $E^{\circ\prime}$ that it is possible that our values of the difference $(\bar{c}_p-\bar{c}_p{}^\circ)$ may be subject to considerable error. On the other hand, we believe the form of the curve to be substantially correct.[12]

An indication of the reliability of our computed thermal quantities was obtained in the following manner: *0.02* mv., which was considered a reasonable estimate for the probable error of the *smoothed values* of $E^{\circ\prime}$, was alternately added to and subtracted from various combinations of successive temperature values of $E^{\circ\prime}$, at a given concentration. These changed values of $E^{\circ\prime}$ were expressed as a function of W and a new set of heat quantities calculated. This distortion of the function of $E^{\circ\prime}$ with respect to T made a difference of *0.1%* in $-AH$ and about 10% in Ac, or $\bar{c}_p{}^\circ$, which appears to be the maximum limit of error for the postulated experimental precision. The reliability of $\bar{L}_2$ is therefore about (266 ± *34) or 13%* at ***0.0005 m*** and about (978 ± *33)* or *3%* at ***0.01 m*** at 25°. The uncertainty in $\bar{L}_2$ at 12.5° is somewhat greater.

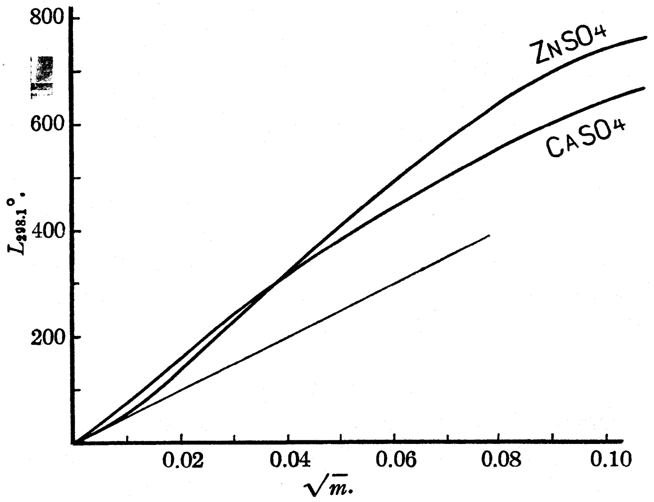

Fig. 3.—Comparison of the heat content of aqueous solutions of calcium sulfate determined calorimetrically by Lange and Monheim and of zinc sulfate determined from e. m. f. measurements by La Mer and Cowperthwaite. The straight line is the limiting law of the Debye–Hückel theory.

In Fig. 3 we have plotted the values of L $(ZnSO_4)$ given in Table IV against the square root of m, along with the experimental values of L for calcium sulfate as determined by Lange and Monheim.[13] The data for zinc sulfate and calcium sulfate are very similar, as would be expected for

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(12) For a critical discussion of the extrapolation of heat capacity data see Gucker. Jr.. and Schminke, THIS JOURNAL, 64, 1358 (1932).

(13) Lange and Monheim. Z. *physik. Chem.*, [Abt. A] 160,349 (1930).

salts of the same valence type, but it is important to point out that in (2,–2) types the individual behavior has not vanished, a point which Lange[14] has repeatedly stressed. Since, as was demonstrated in the previous paper,[3] $\partial a/\partial T$ is zero for zinc sulfate, this individual behavior is most likely to be ascribed to the specific concentration dependence of D and perhaps of V, a problem which has not been satisfactorily investigated as yet for these salt solutions.

It is difficult to compare the reliability of the calorimetric method with the e. m. f. method since the former measures the integral heat of dilution whereas the latter measures the corresponding partial molal quantity. The smoothing of the experimental data which is a necessary preliminary to the numerical differentiation or integration of these quantities for purposes of comparison naturally obscures an answer to the question.

In the e. m. f. measurements the precision of L_2 depends about equally upon the precision with which $(E^{\circ\prime} - E^{\circ})$ and $d(E^{\circ\prime} - E^{\circ})/dT$ can be measured since $E^{\circ\prime}$ is approximately equal to $T\,dE^{\circ\prime}/dT$ in the particular case of zinc sulfate.

There are no measured values of $\bar{c}_p^{\circ}$ for (2,–2) salts with which we may compare our result for zinc sulfate. Rossini[15] calculates values of —68.5 and —73.4 calories per degree per mole for calcium sulfate and barium sulfate, respectively, by combining data for other salts on the basis of the the additivity of ionic partial molal heat capacities at zero concentration. These figures are considerably less than our value. On the other hand, our value of —107 for the (2,–2) salt zinc sulfate is in better agreement with the dependence upon valence type since Randall and Rossini[8] and Rossini[15] find values of —15 to —30 for $\bar{c}_p^{\circ}$ of (1,–1) salts, and values of —50 to —70 for (1,–2) and (2,–1) salts.

Summary

1. Based upon electromotive force measurements of the cell Zn (satd. amalgam), $ZnSO_4(m)$, $PbSO_4(s)$, Pb (satd. amalgam) for the temperatures 0, 12.5, 25, 37.5 and 50° and the concentrations 0.0005, 0.001, 0.002, 0.005 and 0.01 m zinc sulfate the following values have been computed for the reaction Zn (s, satd. with Hg) $+ PbSO_4(s) \longrightarrow ZnSO_4(m) +$ Pb (s, satd. with Hg) in the standard state of unit activity for $ZnSO_4$ at 298.1°K.

$$E^{\circ}_{298.1} = 0.41086 \qquad -\Delta F^{\circ}_{298.1} = 18951 \text{ cal.}$$

$$(dE^{\circ}/dT)_{298.1} = -0.0011220 \qquad -\Delta H^{\circ}_{298.1} = 34380 \text{ cal.}$$

$$(d^2E^{\circ}/dT^2)_{298.1} = -0.000009632 \qquad -\Delta C^{\circ}_{p\,298.1} = 132.4 \text{ cal./deg.}$$

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(14) See Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), for an excellent summary of the work of Lange and collaborators on the calorimetric measurement of heats of dilution in dilute solution, and for a compilation of the temperature coefficients of the dielectric constant of water that can be calculated from the data of various investigators. Later papers by Robinson have appeared in THIS JOURNAL, **54**, 1311 (1932). and (with Hammerschmid), **54**, 3120 (1932).

(15) Rossini, *Bur. Standards J. Research*, **4**, 313 (1930); **7**, 47 (1931)

2. The partial molal heat capacity of zinc sulfate in the standard state (infinite dilution in water) is $\bar{c}_p^\circ$ $ZnSO_4 = -107$ calories per degree per mole.

3. The partial molal heat capacities, the relative partial molal and integral heat contents of zinc sulfate solutions have been computed at each concentration and the results compared with the theoretical formulas derived from the limiting forms of the Debye–Hückel theory using Wyman's determinations for the temperature dependence of the dielectric constant of water.

4. The contribution due to thermal expansion which has been neglected by previous investigators amounts to a correction of **16%** at 25° in the theoretical limiting slope for the concentration dependence of the partial molal heat capacities.

5. The values for the integral heat of dilution of zinc sulfate are compared with the values for calcium sulfate as measured by Lange and Monheim for the same range of concentration. Aside from reasonable individual differences, which have been shown to persist to high dilution, the results are consistent with their valence type.

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The Heat Capacity and Related Thermodynamic Properties of Aqueous Solutions. II. Lithium and Sodium Hydroxides at 25°

BY FRANK T. GUCKER, JR., AND KARL H. SCHMINKE

Introduction

In order to widen the scope of our previous work, we have used the same methods to determine the specific heats of solutions of lithium and sodium hydroxides. The experiments were carried out in the Joule–Pfaundler thermal balance. In the working calorimeter, definite quantities, first of water and then of solution, were balanced against a fixed weight of water in the tare calorimeter. Using a multiple thermel, temperature *differences* were measured with a sensitivity of one or two hundred thousandths of a degree and specific heats were determined with an accuracy of about ±0.01%. The reader is referred to previous articles[1] for detailed descriptions of the apparatus and experimental technique.

Materials and Solutions

The hydroxides were prepared from the best available material, further purified in contact only with platinum, nickel or stainless steel.

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[1] Gucker and Schminke, THIS JOURNAL, 54, 1358 (1932); Gucker, ibid., 50, 1005 (1928); Richards and Gucker. *ibid.*. 47, 1876 (1925).

The preparation of pure lithium hydroxide offered considerable difficulty. Finally it was accomplished in the following tedious but satisfactory way: C. P. lithium chloride was dissolved in absolute alcohol which was saturated with dry hydrogen chloride gas to precipitate out the sodium and potassium salts. The solution was filtered and the alcohol distilled off. The residue of lithium chloride was treated with a slight excess of pure concentrated sulfuric acid and evaporated in a platinum dish until fumes of sulfur trioxide ceased coming off.

C. P. barium hydroxide, recrystallized and drained centrifugally, was dissolved in hot distilled water. The solid lithium sulfate was added to this solution and, on metathesis, yielded a solution about 5 *m* in lithium hydroxide. This was decanted into a paraffin-lined bottle. The voluminous residue of barium sulfate was extracted several times with hot water, to increase the yield of hydroxide. The lithium hydroxide solution was then treated with pure sulfuric acid, a little at a time, until as much as possible of the excess barium ion was removed. The resulting solution contained a negligible quantity of barium and of sulfate ion, and gave equal turbidity when tested with equivalent amounts of either ion. It was found to contain about 0.04 mole per cent. of sodium and less than 0.92 mole per cent. of potassium, since it gave no precipitate with acetic acid and sodium cobaltinitrite solution. The first preparation (Expts. 1–8) contained 0.15 mole per cent. of chloride, which had escaped volatilization in the sulfuric acid treatment. In the second preparation (Expts. 9–15) the chloride ion was removed by treating the lithium sulfate with a small amount of silver sulfate. Any excess silver was removed when the barium hydroxide was added, and remained with the barium sulfate.

The sodium hydroxide was purified by recrystallization of the monohydrate from water solution. About 63 g. of water was added to every 100 g. of sodium hydroxide sticks. A slightly more concentrated solution solidifies completely at room temperature and a less concentrated one gives a low yield of crystals. When the mixture was heated to 60° the solid dissolved completely. The solution was stirred from time to time as it cooled to room temperature, so that it deposited crystals of the right size. These were then drained centrifugally for about ten minutes, to remove the viscous mother liquor as completely as possible. The only impurity which they then contained in appreciable quantities was carbonate, which is always picked up from the air. Fortunately, sodium carbonate is nearly insoluble in concentrated hydroxide and so it is removed quite easily. The crystals were dissolved in the minimum quantity of freshly-boiled distilled water and the resulting solution filtered by suction through a platinum sponge Gooch crucible into a paraffin-lined bottle containing water. The first preparation (Expts. 1–10) was found to contain 0.02 mole per cent. of carbonate, 0.06 mole per cent. of potassium and 0.002 mole per cent. of chloride. The second preparation (Expts. 11–20) was even more completely freed of carbonate. The sodium hydroxide was crystallized as before, then dissolved in the minimum quantity of water and treated with enough recrystallized barium hydroxide to remove all the carbonate. After suction filtration, the excess barium was removed as in the case of the lithium hydroxide. This second solution contained 0.07 mole per cent. of potassium.

All the solutions were made up with freshly-boiled distilled water and were stored in paraffin-lined bottles, whence they were siphoned out as needed through stainless steel or paraffin-lined glass tubes. In order to prevent contamination with carbon dioxide, the incoming air was bubbled through a gas-washing bottle containing some of the same solution.

The analytical methods were more than adequate for our purposes. The solutions were standardized by weight titration against standard hydrochloric acid solutions, using methyl red as indicator. In all but the very dilute solutions, pairs of analyses agreed within a few hundredths of a per cent. The hydrochloric acid solution used for most of the comparisons was 0.61101*m*, as determined by silver chloride residues at the beginning of the work, and 0.61094*m* as determined by comparison with pure sodium carbonate at the end. A 2.15 m hydrochloric acid solution, used for some of the most concentrated alkali solutions, was standardized by silver chloride residues and shown to be consistent with the less concentrated one. The first sodium hydroxide solution was found to be 2.5510m by titration against the first acid solution and 2.5515*m* by titration against the second.

Experimental Results

Tables I and II summarize the experimental results. All the experiments were carried out at an average temperature within a few hundredths of a degree of 25.00°, as determined by a standardized platinum resistance thermometer. Since the temperature coefficient of the specific heat is small, no correction was required in any case and the exact temperature of each experiment is not tabulated. Each series of experiments is numbered chronologically. m is the molality in moles per 1000.0 g. of water. All weights are reduced to the vacuum standard. Ag is the galvanometer deflection when the temperature of the calorimeters has been raised exactly one degree.

The *thermally* ***equivalent*** weight of water in each experiment is determined from the galvanometer deflection in the manner described in our former paper.[2]

Water standardizations made at frequent intervals showed a few individual variations slightly larger than before (amounting to +0.03% in one case and −0.03% in another). Twelve of the experiments, however,

TABLE I

SUMMARY OF RESULTS FOR LITHIUM HYDROXIDE SOLUTIONS AT 25°

Expt.	m	Solution, g.	A mm.	Equiv. wt. of water	Specific ht. s^a	Φ (obsd)	Φ (calcd.)	$\sqrt{m}$
14	0.0404	250.904	+3.4	250.438	0.99814	-22	-18	0.201
15		250.963	+1.2	250.482	.99808	-24		
7	.0900	251.394	+0.7	250.495	.99642	-15.9	-16.2	.300
8		251.374	f1.9	250.468	.99640	-16.1		
5	.1600	252.040	+3.1	250.443	.99366	-15.8	-15.0	.400
6		252.085	f1.4	250.476	.99363	-16.1		
3	.3586	253.756	+0.3	250.502	.98719[1]	-12.11	-12.46	.599
4		253.776	-1.0	250.527	.98721	-12.05		
12	.6418	255.968	+2.0	250.465	.97850	-10.07	- 9.95	.801
13		256.008	+1.8	250.470	.97837	-10.27		
1	1.213	259.657	+3.4	250.437	.96454[2]	-6.13	-6.18	1.101
2		259.647	+3.9	250.426	.96454	- 6.13		
9	2.2728	265.020	-8.1	250.673	.94588[3]	-1.17	-1.09	1.508
10		265.870	-5.7	250.624	.94624	-1.01		
11		265.870	-5.7	250.624	.94624	-1.01		

[a] These values were corrected for the known Cl^- and Na^+ in the solution, assuming linear change of *s* with mole per cent. at any one concentration of OH^-. The corrections were: [1] $+0.1 \times 10^{-4}$; [2] $+0.6 \times 10^{-4}$; [3] 30.1×10^{-4}.

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(2) Gucker and Schminke, THIS JOURNAL. 54, 1358 (1932).

TABLE II

SUMMARY OF RESULTS FOR SODIUM HYDROXIDE SOLUTIONS AT 25°

Expt.	m	Solution, g.	Δg, mm.	Equiv. wt. of water	Specific ht., s[a]	Φ (obsd.)	Φ (calcd.)	$\sqrt{m}$
14	0.0396	251.067	+3.7	250.431	0.99747	−24	−23	0.199
15		251.210	−1.5	250.537	.99732	−28		
16		251.165	−1.6	250.539	.99751	−23		
20[b]		251.200	−1.8	250.545	.99739	−26		
9	.0910	251.905	−1.5	250.537	.99457	−19.9	−21.3	,302
10		251.857	+0.1	250.504	.99463	−19.2		
18	.1635	252.945	+1.8	250.468	.99021	−20.2	−19.5	.404
19		253.025	−1.6	250.541	.99018	−20.5		
7	.2394	253.961	+0.6	250.495	.98635	−17.6	−18.0	.489
8		254.005	−2.5	250.560	.98644	−17.2		
5	.4754	257.067	−1.1	250.529	,97457	−14.51	−14.52	.690
6		257.022	−1.4	250.535	.97476	−14.10		
3	.9999	263.069	−4.5	250.599	.95261[1]	−9.28	−9.10	1.000
4		262.960	+0.4	250.498	.95262	−9.26		
11	1.8261	270.297	−0.2	250.510	.92683[2]	−2.99	−2.96	1.351
12		270.376	−3.2	250.574	.92679	−3.02		
13		270.258	+0.2	250.503	.92693	−2.93		
17		270.196	+6.1	250.381	.92669	−3.07		
1	2.5513	258.945	−9.8	235.736	.91041[3]	+1.31	+1.34	1.597
2		275.150	−1.0	250.527	.91055	+1.37		

[a] These values were corrected for the known K^+ present in the solution, assuming linear change of s with mole per cent. at any one concentration of OH^-. The corrections were: [1] $+0.1 \times 10^{-4}$; [2] $+0.3 \times 10^{-4}$; [3] $+0.4 \times 10^{-4}$.

[b] The solution for Expt. 20 was made up determinate from the 0.1635 m solution and freshly boiled distilled water, in order to check independently the other experiments at the same concentration.

checked as well as before and showed that there was no permanent change from the calibration lines given on page 1363 of our previous article.[2] These were made the basis of our present calculations.

The specific heat, s, is obtained by dividing the equivalent weight of water by the weight of solution taken. The apparent molal heat capacity, Φ, is calculated as before from the equation

$$\Phi = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m}$$

where M_2 is the molecular weight of the solute. The atomic weights used are those of the 1932 table. Since the specific heats are measured at 25°, the values of Φ are in calorie units corresponding to this temperature. The *calculated* values of Φ are obtained from linear equations for Φ against $\sqrt{m}$, derived from the experimental values by the method of least squares. Each value of Φ is given a weight proportional to m, since the error in Φ caused by a given percentage error in s is much larger in dilute than in concentrated solutions.[3]

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(3) Ref. 2, p. 1366.

In Figs. 1 and 2 values of Φ for all the experiments are plotted against $\sqrt{m}$, together with the *calculated* best straight line through these points.

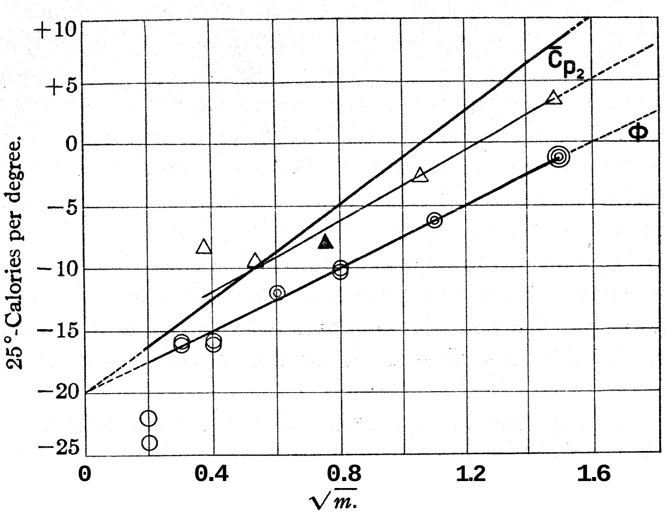

Fig. 1.—Lithium hydroxide: circles, Gucker and Schminke; triangles, Richards and Rowe.

It is evident that in both cases the straight lines represent the data within the experimental error from 0.04 m to over 2 *m*. There is no indication of an upward turn in the dilute end of the curve, at about 0.16 *m*, such as we

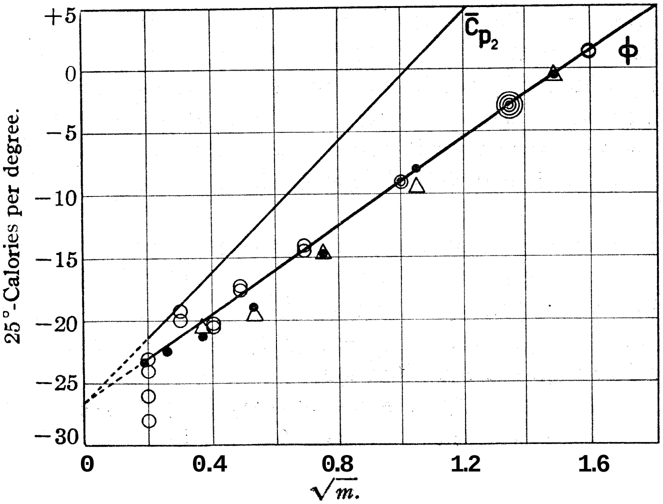

Fig. 2.—Sodium hydroxide: circles, Gucker and Schminke; dots. Richards and Gucker; triangles, Richards and Rowe, recalculated by Richards and Hall.

noted previously in the case of potassium hydroxide and hydrochloric acid, and the lines are continued to zero concentration.

The results for sodium hydroxide are in excellent agreement with the earlier work of Richards and Rowe (as recalculated by Richards and Hall)[4] and of Richards and Gucker.[5] These results (at 18°) are extrapolated to 25° by means of the temperature coefficient between 16 and 20° ($d\Phi/dt = 0.325$) determined by Richards and Gucker for a single solution $NaOH \cdot 25H_2O$ ($\sqrt{m} = 1.49$). Both sets of data were determined from the heat capacity of this same concentrated solution and the temperature coefficient of the heats of dilution of this solution to lower concentrations, using the well-known Person–Kirchhoff relation. The values of Φ are plotted in Fig. 2 and show a *maximum* deviation from our line which corresponds to only 0.07% difference in s (at $\sqrt{m} = 0.745$) for the data of Richards and Gucker and 0.14% (at $\sqrt{m} = 1.05$) for the earlier work of Richards and Rowe.

Our results for lithium hydroxide also agree reasonably well with those of Richards and Rowe[6] which, because of the less satisfactory purity of the material, they state "can hardly be considered as more than preliminary." The values for Φ calculated from their data were extrapolated from 18 to 25°, assuming that the temperature coefficient was the same as that of sodium hydroxide. A glance at Fig. 1 will show that all these values of Φ lie considerably above ours. The line which they define is included for comparison. Its *slope*, which depends only on the temperature coefficient of their heats of dilution, agrees very well with that of ours. The *position* of the line depends wholly on the specific heat of the $LiOH \cdot 100 H_2O$ ($\sqrt{m} = 0.745$), which they measured directly and which is only 0.14% higher than that calculated from our results. The corresponding value of Θ, indicated by the black triangle, lies 2.6 calorie units above our line. If they had measured directly the *most concentrated* solution ($\sqrt{m} = 1.49$) the same percentage difference in s would only have affected Φ by 0.7 calorie unit, and their whole line would have been in much better agreement with ours.

From the equation for the apparent molal heat capacity as a function of the square root of the concentration, it is a simple matter to obtain the partial molal heat capacity of the solute ($\bar{C}_{p_2}$) and the relative partial molal heat capacity of the solvent ($\bar{C}_{p_1} - \bar{C}^\circ_{p_1}$) by the method of Randall and Rossini.[7] The requisite equations are

$$\bar{C}_{p_2} = \Phi + {}^1/_2 m^{1/2} (d\Phi/dm^{1/2}) \qquad \text{and}$$

$$\bar{C}_{p_1} - \bar{C}^\circ_{p_1} = - \frac{\quad}{55.507} \left({}^1/_2 m^{1/} \frac{d\Phi}{d/*} \right)$$

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(4) Richards and Hall, THIS JOURNAL, 61, 734 (1929).

(6) Richards and Gucker, *ibid.*, 51, 722 (1929).

(6) Richards and Rowe, *ibid.*, 43, 781 (1921).

(7) Randall and Rossini, *ibid.*, 51, 323 (1929), and Rossini, *Bur. Standards* J *Research*, *4*, 316, (1930).

Since these quantities are very useful in numerous thermodynamic calculations, we have included them here. The equations which summarize our results for the two solutions are thus found to be

LiOH	NaOH
$\Phi = -19.98 + 12.53\, m^{1/2}$	$\Phi = -26.59 + 17.49\, m^{1/2}$
$\bar{C}_{p_2} = -19.98 + 18.80\, m^{1/2}$	$\bar{C}_{p_2} = -26.59 + 26.24\, m^{1/2}$
$\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1} = -0.1129\, m^{3/2}$	$\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1} = -0.1579\, m^{3/2}$

Summary

We have used the adiabatic twin calorimeter method to determine the specific heats of aqueous solutions of lithium and sodium hydroxides at 25° from 0.04 *m* to over 2 *m*. From these data we have calculated the apparent molal heat capacity of the solutes. When plotted against $\sqrt{m}$ they both give straight lines over the whole range of concentration. Equations are included for the apparent and partial molal heat capacities of the solute and the relative partial molal heat capacity of the solvent. From these it is possible to calculate the heat capacity of these solutions with great precision at any concentration in the range studied.

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Properties of Electrolytic Solutions. III. The Dissociation Constant

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

Experimental data for weak electrolytes in water and for most electrolytes in solvents of lower dielectric constant indicate the existence of an equilibrium of the type

$$A^+ + B^- \rightleftarrows AB \tag{1}$$

In the preceding paper of this series,[1] we have shown that it is possible to describe conductance data (up to moderate concentrations) exactly by means of the mass action equation, provided the influence of interionic forces, in the usual sense of the term, on the thermodynamic properties and mobilities of the ions be taken into account.[2]

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(1) Fuoss and Kraus, THIS JOURNAL, 66, 476 (1933).

(2) It should be pointed out that all terms in activity and migration velocity of higher order than $c^{1/2}$ in concentration are necessarily included in our dissociation constants derived from conductance data. Since the method of calculation is applied only to low (ion) concentrations, we believe that our K describes primarily the effect which we are naming mass action, *i. e.*, the formation of electrically neutral structures from ions. It is evident, both on experimental and theoretical [Kramers, *Proc.* Amsterdam. **30**, 145 (1927)] grounds that some *specific* interaction between ions of opposite charges must be considered in addition to the interionic effect described by Debye's time–average potential The specific interaction is most simply treated by means of arguments based on Equation (1).

The relative concentration of ions was defined as the fraction of the total solute free to carry the current in the conduction process, and the concentration of undissociated molecules was determined by difference. It was assumed that the undissociated molecules were normal in their thermodynamic behavior and that the dielectric constant of the solution was that of the pure solvent. These assumptions appeared to be justified by the results obtained in accounting for conductance data.

It is our present purpose to discuss the mechanism underlying (1) and to compare our results with experimental data. We assume that the ions in a solution may be treated as uniformly charged spheres which, on account of solvation, are presumably larger than the corresponding gaseous ions. The electrostatic forces between ions will cause ions of unlike charges to attract one another, and for any pair of ions the mutual potential energy as a function of distance is given by Coulomb's law. If two unlike ions "approach to contact," a definite amount of energy is required to separate them; if this energy is much less than the kinetic energy of the solvent molecules, thermal agitation will soon dissociate the ion pair, while if the energy is considerably greater, the ion pair has a good chance of existing for some time. These considerations permit us to express the energy and hence the dissociation constant of an electrolyte in terms of the size of the ions involved and the dielectric constant of the solvent.

A similar calculation has been made by Bjerrum,[3] and applied to electrolytes in solvents of fairly high dielectric constant. The ion sizes calculated from activity data seem somewhat small, and it is quite possible that ion sizes so determined include other effects than association. In view of Bjerrum's result that electrolytes with sum of radii greater than 3.5×10^{-8} cm. will not associate to any great extent in water, combined with ideas of ion sizes derived from other sources, it seems quite probable that most salts are completely dissociated in water. It is only in solvents of lower dielectric constant, where the Coulomb energy is correspondingly greater, that an ion pair has sufficient energy to be stable. Also, in solvents of lower dielectric constant, the fraction of solute associated is sufficiently great to permit its accurate determination by means of conductance experiments.

In this paper the dissociation constant, calculated on the hypothesis of Coulomb forces, will be derived as an explicit function of the dielectric constant of the solvent and of a parameter a, the "ion size." The results have been compared with experimental data covering a variety of salts and solvents. Particular attention has been given to the dependence of dissociation constant on dielectric constant; this has been investigated over a range of dielectric constant from 2.4 to 40. The calculated dissociation energies agree with experimental values very closely over the entire range.

(3) Bjerrum, *Kgl. Danske Vidensk. Selskab.*, *7*, No. 9 (1926); Falkenhagen, "Electrolyte." Verlag von S. Hirzel, Leipzig, 1932, p 267 ff.

II. The Dissociation Constant

We are given a binary electrolyte dissolved in a volume V of solution. Let there be N ions of each charge, so that the number of ions per cubic centimeter, n, equals N/V. Then, if a positive ion with charge $+e$ is in a volume element dv_1, the probability that a negative ion with charge $-e$ will be in a volume element dv_2 at a distance r_{12} from dv_1 is

$$\mathbf{P} = n \exp\left(\frac{e^2}{r_{12}DkT}\right) dv_1 dv_2$$

where D is the dielectric constant, k is Boltzmann's constant, and T is the absolute temperature. In spherical coordinates, with the origin at the first ion, this is

$$\mathbf{P} = n \exp\left(\frac{e^2}{rDkT}\right) r^2 \sin\theta \, d\theta \, d\varphi \, dr \, dv_1$$

If we keep the positive ion fixed, **P** has a minimum at a distance

$$r_{min} = q = e^2/2DkT \tag{2}$$

The energy required to separate the two ions at a distance q is $2kT$, four times the mean thermal energy per degree of freedom. This result was first obtained by **Bjerrum.**[3] Two ions at a distance $r < q$ are to be considered as an associated ion pair. We may then determine[4] the free energy ψ associated with the reaction

A+ + B ' A B

by evaluating the phase integral for the system

$$Ne^{-\psi/kT} = n \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \int_a^q \exp\left(\frac{e^2}{rDkT}\right) r^2 \, dr \int_v dv_1$$

where the positive ion is allowed to be anywhere in the volume V, and the negative ion ranges over the sphere between r = a (contact) and $r = q$ (dissociation). Substituting a new variable of integration

$$y = e^2/(DkTr)$$

and performing the integration, we obtain

$$e^{-\psi/kT} = 4\pi \left(\frac{e^2}{DkT}\right)^3 \int_2^b e^y \, y^{-4} \, dy \tag{3}$$

The definite integral

$$Q(b) = \int_2^b e^y \, y^{-4} \, dy \tag{4}$$

is a function of

$$b = e^2/aDkT \tag{5}$$

that is, depends on the ion size and the dielectric constant of the solvent. The conventional mass action constant K is expressed in terms of concentrations in equivalents per liter; if we consider one equivalent of each species of ions, $nV = N = 6.06 \times 10^{23}$, Avogadro's number, and we have the following relation between ψ and K

$$N\psi = RT \ln (1000 \, K/N)$$

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(4) **Tolman,** "Statistical Mechanics," Chemical Catalog Co., New **York,** 1927, **p.** *307.*

Substituting in (3), our final result is

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)^3 Q(b) \tag{6}$$

The values of the function $Q(b)$ have been tabulated by Bjerrum for $1 \leqslant b \leqslant 15$. (The function $Q(b)$ has no physical significance for $b < 2$ because $b = 2$ corresponds to the limiting case of complete dissociation when $a = q$). This range of b values was insufficient for our calculations; a further range of values is given in Table I.

TABLE I

LOG $Q(b) \approx 0.4343b - 4$ LOG $b +$ LOG $(1 + \delta)$

b	log $Q(b)$	b	log $Q(b)$
15	1.96	40	11.01
17	2.59	50	14.96
20	3.59	60	18.98
25	5.35	70	23.05
30	7.19	80	27.15

The values given in Table I are approximate. The expansion of $Q(b)$ is

$$Q(b) = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\}$$

and the available tables[6] for the integral exponential $Ei(x) = \int_{\infty}^{-x} e^{-u}u^{-1}\,du$ run only to $x = 15$. We therefore used the asymptotic expansion

$$Ei(x) \sim \frac{e^x}{x}\left(1 + \frac{1!}{x} + \frac{2!}{x^2} + \frac{3!}{x^3} + \dots\right)$$

in order to compute $Ei(b)$ for $b > 15$, and in taking the logarithm, $(1/6)\{e^2 - Ei\ (2)\} = 0.41$ was neglected in comparison with the other terms. This gives

$$\log Q(b) \approx 0.4343\,b - 4\log b + \log(1 + 6)$$
$$\delta = \frac{4}{b} + \frac{4.5}{b^2} + \frac{4.56}{b^3} + \dots$$

These approximations cause an error of several per cent. in log $Q(b)$ for b equal to 15, but this error decreases rapidly as b increases.

If the dissociation constant of an electrolyte is known, $Q(b)$ is determined by (6). From a graph of $Q(b)$ against b, the corresponding value of b is obtained, and then a is evaluated from (5). Conversely, if a is known, K may be computed.

The functional relation (6) between the dissociation constant of an electrolyte and the dielectric constant of the solvent shows that K must decrease very rapidly as D decreases. If we retain only the first term of the asymptotic expansion, we have, approximately

$$1/K \approx \frac{4\pi N}{1000}\,a^3\,\frac{aDkT}{e^2}\exp\left(\frac{1}{a}\,\frac{e^2}{DkT}\right) \tag{7}$$

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(5) Jahncke and Emde, "Funktionentafeln," Teubner, 1909.

so that $1/K$ increases very much like e^b/b. Since $(-kT \log K)$ measures the work done against the Coulomb forces on separating a pair of ions from contact ($r = a$) to the distance ($r = q$) at which their thermal motion has an even chance of carrying them further apart, we may interpret (6) as a relation between the dissociation energy of an ion pair and the dielectric constant of the medium. It should be noted that K is extremely sensitive to the value of a when D is small, as is shown in (7).

Equations (6) also contains the statement that, for a given salt, dissociation is compiete in solvents having a dielectric constant above a definite value. When the distance at contact is equal to (or greater than) q, the Coulomb forces no longer suffice to render an ion pair stable and then the only interaction between ions is that described by the usual "ion atmosphere." The condition $a = q$ is equivalent to $b = 2$ and $Q(b) = 0$. For example, for a salt with $a = 6.40 \times 10^{-8}$, K increases with increasing dielectric constant until at $D = 41.4$, $K = 1$. Beyond this value of D, K increases very rapidly and the limit $K = \infty$ corresponds to $D = 43.6$ where $b = 2$. In other words, on a $(-\log K)$–D plot, the $(-\log K)$ curve crosses the axis at $D = 41.4$ and becomes asymptotic to a vertical line at $D = 43.6$. In solvents of higher dielectric constant, there can be no ion association. For a given solvent, there is likewise a maximum value of a above which electrolytes do not form ion pairs; for example, in water at 25°, this critical value of a is about 3.5×10^{-8} cm.

It is to be expected that a will depend on the atomic properties of the constituent ions of the electrolytes. But there is considerable evidence indicating that the ions are solvated, *i. e.*, that each ion is surrounded on the average by a certain number of solvent molecules which accompany the ion in question. (This average number need not, of course, be integral.) consequently, the value of a may also depend on the atomic properties of the solvent. In general, we might except that the more intense the field around an ion, the greater will be the value of a. If two solvated ions approach within a distance $r < q$, they probably will approach to "contact" and will form an ion pair (which will eventually be dissociated by a high speed collision). As an approximate model of the solvated ion, we may picture the central ion as a small sphere carrying a charge $\pm$ e, surrounded by several shells of solvent molecules, the inner shells firmly bound and the outer layers less and less firmly held (or, better, oriented with respect to the central ion), until at a moderate distance from the center a solvent molecule has a good chance of assuming a random orientation. On this basis, as two ions form an ion pair, it seems reasonable to suppose that the center to center distance a of the ion pair will be less than the sum $(r_1 + r_2)$ of the radii of the freely migrating ions, because the effective dielectric constant of the polarized solvate shell around each ion is certainly less than the macroscopic dielectric constant, and the Coulomb forces are correspondingly increased. The ions may indeed approach so closely that the assumed spherical symmetry of the charge of the central ion no longer obtains. The mechanism of the ion-pair formation as here pictured is undoubtedly over-simplified; nevertheless, it provides a tentative working scheme which appears to be in agreement with the facts available.

III. Comparison with Experiment

Influence of the Dielectric Constant.—We shall first consider the dissociation constant of tetraisoamylammonium nitrate. The conductance of this salt has been measured at 25° in dioxane, water, and in a series of mixtures of dioxane and water covering the dielectric constant range 2.2 to 80.[6]

In water, the salt is a strong electrolyte. The conductance in the dilute region is nearly linear against the square root of concentration, and extrapolation by Onsager's method gives $\Lambda_0 = 86.9$. This small value of Λ_0 indicates a rather large ion size, which, indeed, might be expected for a salt of this structure. Despite the fact that the observed conductance curve approaches its limiting tangent from below, we are inclined to consider the salt as completely dissociated in water and to ascribe the negative deviations to causes other than incomplete dissociation?

In a mixture of dioxane and water containing 53% water, with a dielectric constant of 38.0, the $\Lambda-\sqrt{c}$ curve is nearly parabolic at concentrations below 0.002 N. The viscosity of dioxane–water mixtures has been determined[8] at 20 and 40° for several compositions. We have interpolated values for our mixtures at 25° in order to evaluate the coefficient of the square root term in the conductance equation. Using Onsager's approximate equation

$$\Lambda = \Lambda_0 - \alpha\sqrt{c} - (\Lambda_0/K)\,c$$

we obtain $\Lambda_0 = 42.8$ and $K = 0.28$. Using $\Lambda_0 = 42.8$ and $\alpha = 69.5$, and computing K for several higher concentrations by means of equations (2), (3) and (7) of our previous paper,' where $\beta = 1.51$ and $\delta = 1.0$, we obtain the following results: $c = 0.00748, 0.00441$; $\Lambda = 36.32, 37.72$; $\gamma = 0.9865, 0.9875$; $f = 0.759, 0.806$; $K = 0.31, 0.21$, av. 0.26.

The values of the constants Λ_0 and K for the mixtures containing 20.2 and 14.95% water were obtained by our intercept method. The specific and derived constants are as follows: water content = 20.2, 14.95; $D = 11.9, 8.5$; $\eta = 0.0174, 0.0161$; $\beta = 8.6, 13.5$; $\Lambda_0\delta = 79, 100$; $\Lambda_0 = 34, 31$; $K = 9.0 \times 10^{-4}, 1.00 \times 10^{-4}$.

For lower concentrations of water, we have no data at electrolyte concentrations sufficiently low to permit the application of the intercept

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(6) Kraus and Fuoss, THIS JOURNAL, 55, 21 (1933).

(7) Onsager, *Physik. Z.*, 28, 296 (1927).

(8) Herz and Lorentz, *Z. physik. Chem.*, 140, 407 (1929).

method of determining Λ_0 and K. The ion concentrations are quite small on account of the low dissociation, so that the interionic terms may be estimated with fair accuracy; the difficulty is that the effect which eventually produces a minimum in the conductance curve causes deviations from our equations which prevent extrapolation for Λ_0. At concentrations well removed from the minimum, we may make a good estimate of K if we assume a reasonable value of Λ_0 (based on viscosity) and estimate the corrections due to interionic effects. For the present, the deviations due to the minimum will be neglected; in the concentration range used below to calculate K this is justified. In the next paper of this series, the situation at the minimum point will be considered.

The mixture containing 9.5% water has a dielectric constant of 5.84 and a viscosity of 0.0161. Assuming $\Lambda_0 = 30$, $\alpha = 473$, $\delta = 4.5$, $\beta = 25$, we obtain the following: $c \times 10^4 = 0.835, 1.378, 2.66, 4.01$; $A = 4.53, 3.74, 2.90, 2.48$; $\gamma = 0.1605, 0.1336, 0.1055, 0.0915$; $f = 0.815, 0.785, 0.743, 0.715$; $K \times 10^6 = 1.69, 1.74, 1.82, 1.89$. The increase of K with increasing concentration is due to the neglected influence of the minimum, which makes the conductance greater than it would otherwise be. Extrapolating the above values of K to zero concentration in order to eliminate this error, we obtain $K = 1.65 \times 10^{-6}$ for $D = 5.84$. Similar calculations for the other mixtures containing smaller amounts of water lead to the values of $\log K$ given in Table II.

TABLE II

CONSTANTS FOR **TETRAISOAMYLAMMONIUM** NITRATE IN DIOXANE–WATER MIXTURES

% Water	D	$-\log K$	K	E, cal.	$a \times 10^8$
0.60	2.38	15.7	2×10^{-16}	21,400	6.01
1.24	2.56	14.0	1×10^{-14}	19,100	6.23
2.35	2.90	12.0	1×10^{-12}	16,400	6.36
4.01	3.48	9.6	2.5×10^{-10}	13,100	6.57
6.37	4.42	7.53	3.0×10^{-8}	10,300	6.65
9.50	5.84	5.78	1.65×10^{-6}	7,900	6.45
14.95	8.5	4.00	1.00×10^{-4}	5,450	6.50
20.2	11.9	3.05	9.0×10^{-4}	4,150	6.70
53.0	38.0	0.60	0.25	820	6.15

In the fourth column are given the values of K and in the fifth column the corresponding energies, $E = -RT \ln K$, the dissociation energies per gram molecule. It will be noted that in solvents of low dielectric constant the dissociation energy reaches values comparable with those of ordinary reactions.

On substituting values for the constants in (6), we obtain for 25°

$$K^{-1} = 1.320 \times 10^6 D^{-3} Q(b)$$

whence

$$-\log K = 6.120 + \log Q(b) - 3 \log D \tag{8}$$

By means of (8), $\log Q(b)$ is determined, and from a graph of this function against b, values for b are obtained. These, substituted in (5), together with the appropriate dielectric constants, yield the values of *a* tabulated in the sixth column of Table II.

In the various dioxane–water mixtures considered above, the molar water concentration was always greatly in excess of the salt concentration. Furthermore, in view of the high polar moment of water, it seems reasonable to assume that the solvate molecules would be predominantly water, and that the relative hydration of the solute ions would be more or less independent of the absolute water concentration at the high water concentrations involved. In this event, we might expect that *a* would be the same for any mixture of dioxane and water. This is actually the case as is shown in Table II, the extreme variation being only 10%.

Using the average value, $a = 6.40 \times 10^{-8}$ cm., we may compute the dissociation constant of tetraisoamylammonium nitrate in any mixture of dioxane and water by means of equations (4), (5) and (6). The result of this calculation is shown in the accompanying figure, where (−log K) is plotted against log D. The circles represent the experimental values. The agreement between the observed values and those calculated on the basis of a *single* value of *a* is satisfactory over a range of fifteen powers of ten in the constant K. It is interesting to note that no association of the type described by our equations is possible for tetraisoamylammonium nitrate in mixtures having a dielectric constant greater than 43.6, where the curve tends to $1/K = 0$ ($\log K = \infty$).

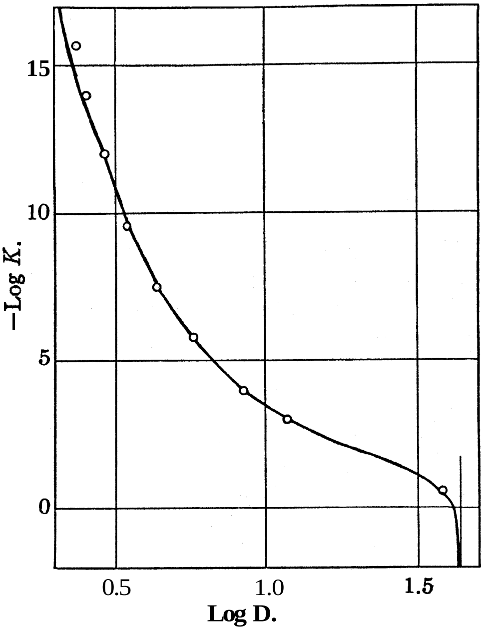

Fig. 1.—Dissociation constants for tetraisoamylammonium nitrate in dioxane–water mixtures. Solid curve calculated, circles observed.

Influence of the Solvent Medium.—The same electrolyte in different solvents will have different values of *a*, if this parameter depends on the solvent as well as on the solute. We have applied the intercept method to the conductance data for solutions of silver nitrate in the following solvents: acetonitrile at 25°,[9] benzonitrile at 25°,[10] and ammonia at −33°.[11] The

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(9) Walden and Birr, *Z. physik. Chem.*, **144**, 269 (1929).

(10) Martin, *J. Chem. Soc.*, 3270 (1928).

(11) Franklin and Kraus, *Am. Chem. J.*, 98,277 (1900); THIS JOURNAL, **27**, 191 (1905).

constants for these systems were obtained by extrapolation of the conductance data by the method previously described by us.'

The values of Λ_0 and $(-\log K)$ thus obtained are given in Table III in the first and second columns; the values of a calculated from the dissociation constant by means of (4), (5) and (6) are given in the third column; the dielectric constants and polar moments of the solvents[12] are given in the last two columns.

TABLE III

CONSTANTS FOR SILVER NITRATE IN DIFFERENT SOLVENTS

Solvent	Λ_0	$-\log K$	$a \times 10^8$	D	$\mu \times 10^{18}$
Benzonitrile	55.2	3.495	1.62	25.2	3.91
Acetonitrile	186	1.775	1.90	36	3.11
Ammonia	291	2.314	5.78	22	1.49

It will be noted that a varies from solvent to solvent, and that, while neither log K nor a changes in the same order as D, a decreases as the electrical moment of the solvent increases. Although the values of a for the nitriles seem somewhat small, the results are in accord with what might be expected of silver nitrate in these solvents. Ammonia forms a very stable complex with silver ion, even in water. Hence, in ammonia, the positive ion is relatively large, and solvation, in the sense of solvent dipoles oriented by the ionic field, further increases the effective radius. The result is that silver nitrate is a much stronger electrolyte in ammonia of dielectric constant 22 than in benzonitrile of dielectric constant 25

Influence of the Ions.—Finally we shall consider a series of different salts in the same solvent: the nitrates of the alkali metals in liquid ammonia at $-40°$.[13] The constants are given in Table IV. The single conductances are computed on the basis of Franklin and Cady's[14] transference data which give $\Lambda(NO_3)/\Lambda(K^+) = 1.006$ at $-33°$.

TABLE IV

CONSTANTS FOR THE ALKALI METAL NITRATES IN AMMONIA AT $-40°$

Salt	Λ_0	$K \times 10^4$	$a \times 10^8$	Ion	Λ_0 (ion)	$r^* \times 10^8$
$LiNO_3$	277	36.5	5.04	Li^+	112	0.28
$NaNO_3$	295.1	28.84	4.46	Na^+	130.1	0.41
KNO_3	329.0	14.71	3.57	K^+	164.0	0.82
$RbNO_3$	341.8	11.41	3.34	Rb^+	176.8	1.20
$CsNO_3$	333.5	9.66	3.21	Cs^+	168.5	1.48

For this series the variation of the dissociation constant is perfectly regular; the salts become weaker electrolytes (K and hence a decrease) as the atomic number of the cation increases. This indicates a decreasing solvation as the size of the external electron ring in the alkali metal ion

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(12) Smyth, "Dielectric Constant and Molecular Structure." Chemical Catalog Co., New York, 1931.

(13) Monosson and Pleskow, Z. *physik. Chem.*, **A156**, 176 (1931).

(14) Franklin and Cady, This JOURNAL, 26, 499 (1904).

increases, that is, as the external field due to the single excess charge in the nucleus of the ion becomes progressively weaker and consequently exerts less force on the solvent dipoles. This is also shown by the ion conductances, which increase regularly from lithium to rubidium. The reversal from rubidium to cesium does not appear surprising in view of the fact that the radius r^* of the external electron shell in the alkali ions, as calculated by Pauling,[15] changes but little in going from rubidium to cesium. The solvation is apparently about the same for the two ions, and the net sphere equivalent to the cesium ion plus solvate is a little larger than that for rubidium. No values for radii calculated from Λ_0 are given, because the equations of motion of a charged particle in a dipole liquid are not yet known with sufficient certainty.[16]

In the light of the foregoing discussion, it appears that the application of Coulomb's law to the (binary) ionic equilibrium in solvents of widely varying dielectric constant accounts for the change of dissociation constant with dielectric constant within the limit of experimental error. The function connecting K and D involves only a single disposable parameter a, of the nature of a distance. The value of this parameter depends on the constituent ions of the electrolyte, and, for a given electrolyte, on the properties of the solvent medium. For mixtures of dioxane and water a has a constant value. The results of the present investigation therefore lend support to the view that the so-called mass action effect is primarily controlled by Coulomb forces between the ions.

Summary

1. Bjerrum's ion-pair model for undissociated molecules of electrolytes in solution gives a physical picture which agrees well with observed conductance data.

2. The dissociation constant of a binary electrolyte is a function of the dielectric constant of the solvent, and can be evaluated numerically if the value of a parameter a is given.

3. The parameter a depends on the atomic properties of solute and solvent, and is roughly an additive function of the constituent ions.

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(15) Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927).

(16) M. Born, *Z. Physik*, **1**, 221 (1920); H. Schmick, *ibid.*, **24**, 66 (1924).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 27]

Thermodynamic Properties of Fused Salt Solutions. VII. Zinc Bromide in Lead Bromide

BY EDWARD J. SALSTROM

The investigation herein described represents a continuation of a series of studies on the thermodynamics and free energies of fused salt solutions begun by Hildebrand.[1] Unlike this initial work, where the chlorine electrode was formed by a polarization method, the bromine electrode utilized by the author has been produced by bubbling electrolytic bromine vapor over a graphite rod dipping into the cell melt as previously described.[2]

The lead bromide used in the cells, and as a source of bromine, was prepared by precipitation with a slight excess of "c. P." hydrobromic acid from a lead acetate solution. The precipitate was repeatedly washed by decantation with a very dilute solution of the acid, then dried, first by suction and finally at 150° in a furnace for twenty-four hours. The zinc bromide, obtained from commercial sources of highest purity, was fused to partially free it from water. Final traces of moisture were removed from the cell by bubbling dry hydrogen bromide gas through the melt for an hour and a half. The lead used as the negative electrode was prepared by the electrolysis of lead bromide which had been similarly freed from moisture and hydrolysis products. The composition of the cell contents was determined after the run by converting the bromides to sulfates, in which form the lead was weighed.[3]

The results of the e. m. f. measurements are given in Table I and are shown graphically in Fig. 1. The values for pure lead bromide are the results of four separate cells, three of which are indicated in the figure by points of different type and were run at Berkeley.[2] The mean deviation of the points from a straight line in Fig. 1 is less than 0.2 mv. while the maximum deviation is 1.0 mv.

The fluctuations of these Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), Br_2(g.), cells were found to be more marked than those for any of the previous systems studied by the author. More than usual fluctuations were also found in the cell, Zn(liq.), $ZnBr_2$(liq.), Br_2(g.), while cells of Cd(liq.), $CdBr_2$(liq.), Br_2(g.) could not be measured due to metal fogs forming in sufficient amount to short the cell soon after the hydrogen bromide gas had been shut off and bromine bubbling begun. Thus it is likely that slight formation of metal fog by zinc may be responsible for this unsteadiness.

Reproducible cells for 0.9 mole fraction of zinc bromide in lead bromide

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(1) Hildebrand and Ruhle, THIS JOURNAL, 49, 722 (1927).

(2) Salstrom and Hildebrand, *ibid.*, 63. 4641 (1930).

(3) Cf. Treadwell-Hall, "Aaalytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York. 1919. p. 174.

TABLE I

E. M. F. VALUES OF THE CELL, Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), Br_2(g.)

Temp., °C.	E. m. f. obs., volts
Cell A(N_1 = 1.000)	
423.2	1.0788
438.3	1.0692
443.5	1.0665
450.5	1.0624
451.0	1.0615
453.0	1.0601
465.6	1.0525
468.0	1.0516
478.1	1.0461
484.3	1.0416
496.2	1.0330
501.1	1.0306
510.4	1.0265
517.1	1.0215
520.0	1.0200
527.6	1.0156
530.6	1.0136
532.5	1.0017
Cell B(N_1 = 0.902)	
400.6	1.0945
425.0	1.0798
425.9	1.0792
452.6	1.0635
453.3	1.0632
475.4	1.0500
494.3	1.0384
506.8	1.0311
Cell C(N_1 = 0.794)	
403.2	1.0971
433.7	1.0786
434.6	1.0783
454.9	1.0662
468.9	1.0580
478.7	1.0520
Cell D(N_1 = 0.704)	
395.1	1.1041
396.3	1.1040
426.5	1.0862
444.3	1.0759
469.2	1.0608
471.0	1.0607
497.4	1.0454
508.2	1.0389
Cell E(N_1 = 0.604)	
402.6	1.1046
416.8	1.0959
417.1	1.0957
442.4	1.0817
442.6	1.0815
466.7	1.0674
479.7	1.0603
491.0	1.0532
491.2	1.0530
511.2	1.0424
Cell F(N_1 = 0.486)	
401.9	1.1104
402.2	1.1101
424.0	1.0977
424.9	1.0974
450.4	1.0821
450.7	1.0819
473.3	1.0697
496.1	1.0571
513.8	1.0471
514.1	1.0470
Cell G(N_1 = 0.392)	
405.7	1.1123
406.2	1.1122
428.7	1.1000
456.8	1.0850
470.7	1.0771
496.1	1.0632
518.1	1.0516
Cell H(N_1 = 0.288)	
403.5	1.1193
419.8	1.1107
420.0	1.1110
452.3	1.0946
475.3	1.0826
511.8	1.0639
Cell I(N_1 = 0.210)	
392.1	1.1306
408.7	1.1223
418.7	1.1175
437.1	1.1091
438.6	1.1087
442.6	1.1072
445.9	1.1055
474.1	1.0917
501.9	1.0789
Cell J(N_1 = 0.200)	
429.1	1.1143
429.3	1.1142
454.6	1.1022
475.6	1.0926
505.3	1.0782
516.6	1.0737

could not be obtained. Analysis of the lead electrode removed from these cells showed traces of zinc. In cells of 0.8 mole fraction of zinc bromide no such traces of zinc were found in the lead and reproducible results were obtained. The author has calculated the free energy of the reaction, Pb + $ZnBr_2$ = $PbBr_2$ + Zn, to be +10,990 cal. at 500° using an unpublished value of 1.2702 volts for the e. m. f. of the cell, Zn(liq.), $ZnBr_2$(liq.), Br_2(g.), obtained in this Laboratory. The analysis showed, and this value seems to indicate, that displacement of zinc from zinc bromide by lead does not take place at or below 0.8 mole fraction of zinc bromide.

To determine if the molal volume of the solution differs from additivity, density measurements were made upon pure zinc bromide and upon a half mole fraction solution of zinc bromide and lead bromide. The method was similar to that previously described.[4] The results are shown in Table II and the values for zinc bromide and the solution may be represented by the equations, $d^t = 3.776 - 0.000913t$ and $d^t = 5.086 - 0.001248t$, respectively.

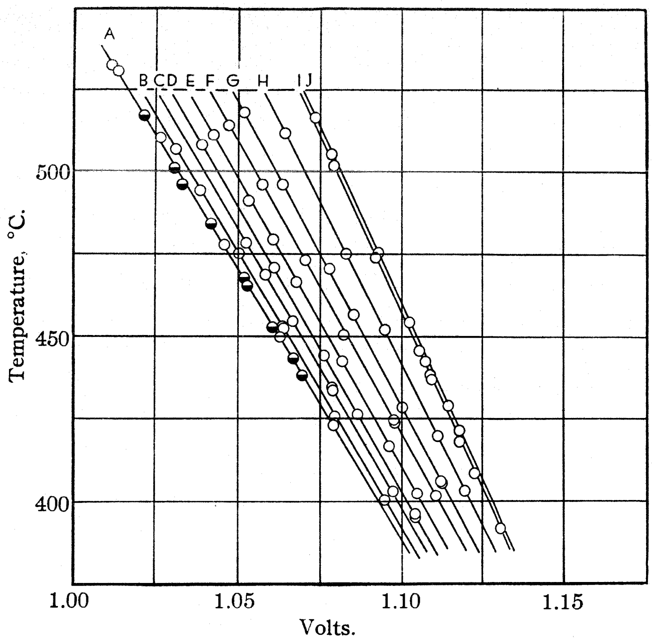

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Pb, $PbBr_2$, $ZnBr_2$, Br_2. Mole fractions of lead bromide are shown in Table I.

TABLE II

DENSITIES OF LIQUID ZINC BROMIDE AND OF ITS SOLUTION WITH LEAD BROMIDE

100% $ZnBr_2$		100% $ZnBr_2$		50% $ZnBr_2$, 50% $PbBr_2$		50% $ZnBr_2$, 50% $PbBr_2$	
Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
407.0	3.405	462.3	3.354	401.9	4.585	469.2	4.501
409.9	3.402	483.6	3.334	408.5	4.576	488.6	4.476
423.9	3.389	499.7	3.320	423.6	4.558	505.7	4.455
435.9	3.378	512.0	3.309	440.0	4.538	521.8	4.435
448.9	3.364			453.0	4.521		

Using the density values for lead bromide previously obtained by the author,[2] the molal volumes of lead bromide and zinc bromide have been calculated to be 67.05 and 67.85 cc., respectively, at 500° while at 400°

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(4) Salstrom, This JOURNAL, 54, 2653 (1932)

their respective volumes are 65.60 cc. and 66.03 cc. The volumes of a mole of solution were found to be 66.36 cc. at 500° and 64.56 cc. at 400°. Thus the observed solution volumes differ from additivity by being 1.09 cc. less at 500° and 1.26 cc. less at 400°.

Since the chief interest lies in the relation of free energy to composition at constant temperature, Fig. I was made upon a large scale, and the values for the e. m. f.'s at each composition determined at the temperatures, 400, 450 and 500°. From these have been calculated the free energy of formation of lead bromide from molten lead and bromine vapor, ΔF_1, the free energy of dilution or the partial molal free energy, $\bar{F}_1$, the temperature coefficient, dE/dT, the entropy change, ΔS_1, the partial molal entropy, $\bar{S}_1$, the heat of formation, ΔH_1, the partial molal heat, $\bar{H}_1$, the activity of lead bromide in the solutions, a_1, taking pure lead bromide as the standard state, and the activity coefficient of lead bromide, γ.

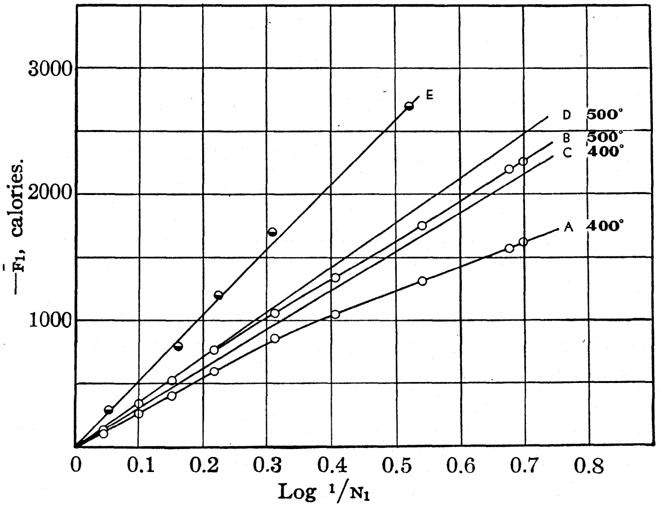

Fig. 2.—Variation of free energy of dilution of lead bromide with composition. Curve E is for $PbCl_2$–$ZnCl_2$ at 500°.

These values are given in Table III, and Fig. 2 curves A and B show the free energy of dilution of lead bromide, $-\bar{F}_1$, plotted against log $1/N_1$ at the temperatures of 400 and 500°, respectively, where N_1 is the mole fraction of lead bromide.

These curves may be compared with those predicted by Raoult's law which assumes that $a_1 = N_1$. In this case, the assumption of no ionization, or of complete ionization of both salts with no change in the interionic forces, makes no difference since in the latter case dilution with zinc bromide would make no change in the proportion of the bromide ion, the only effect being a substitution of lead ion by zinc ion reducing the activity of the former and hence of lead bromide in proportion to N_1. Such calcu-

TABLE III

THERMODYNAMIC PROPERTIES OF LEAD BROMIDE DILUTED WITH ZINC BROMIDE

N_1	1.000	0.902	0.794	0..04	0.604	0.486	0.392	0.288	0.210	0.200
dE/dT, mv./deg	−0.607	−0.599	−0.590	−0..80	−0.571	−0.564	−0.542	−0.511	−0.470	−0.469
$\Delta \bar{S}_1$, cal./deg.	−28.0	−27.6	−27.2	−22.8	−26.4	−26.0	−25.0	−23.6	−21.7	−21.6
$\bar{S}_1$, cal./deg.	0	0.4	0.8	.2	1.6	2.0	3.0	4.4	6.3	6.4
400° E	1.0928	1.0951	1.0986	1. 116	1.1058	1.1114	1.1155	1.1211	1.1268	1.1279
400° $\Delta \bar{F}_1$	−50430	−50540	−50700	−5 040	−51030	−51290	−51480	−51740	−52000	−52050
400° $\bar{F}_1$	0	−110	−270	−10	−600	−860	−1050	−1310	−1570	−1620
400° $\Delta \bar{H}_1$	−69270	−69140	−69020	−[illegible] 850	−68800	−68790	−68310	−67610	−66600	−66590
400° $\bar{H}_1$	0	130	250	20	470	480	960	1660	2670	2680
400° a_1	1.000	0.921	0.817	0.736	0.639	0.526	0.456	0.376	0.309	0.298
400° γ	1.00	1.02	1.03	1.05	1.06	1.08	1.16	1.30	1.47	1.49
450° E	1 [illegible]4	1.0652	1.0691	1.0726	1.0772	1.0832	1.0884	1.0956	1.1030	1.1045
450° $\Delta \bar{F}_1$	−[illegible]0	−49160	−49340	−49500	−49710	−49990	−50230	−50560	−50910	−50970
450° $\bar{F}_1$	0	−130	−310	−470	−680	−960	−1200	−1530	−1880	−1940
450° a_1	1.000	0.914	0.806	0.721	0.623	0.513	0.434	0.345	0 270	0.259
450° γ	1.00	1.01	1.02	1.02	1.03	1.06	1.11	1.20	[illegible]	1.30
500° E	1.032	1.0352	1.0396	1.0436	1.0487	1.0550	1.0613	1.0700	1.0798	1.0810
500° $\Delta \bar{F}_1$	−47630	−47770	−47980	−48160	−48400	−48690	−48970	−49380	−49830	−49890
500° $\bar{F}_1$	0	−140	−350	−530	−770	−1060	−1340	−1750	−2200	−2260
500° a_1	1.000	0.913	0.796	0.708	0.606	0.502	0.418	0.320	0.239	0.230
500° γ	1.00	1.01	1.00	1.01	1.00	1.03	1.07	1.11	1.14	1.15

lations give at 400 and 500° curves C and D, respectively. Thus it is seen that at the higher temperature, curve B, agreement is very good up to 0.6 mole fraction of lead bromide. Beyond this point a small but increasingly positive deviation takes place. At the temperature of 400°, curve A, there is considerably greater positive deviation from Raoult's law which persists throughout the entire range of composition. This can be seen with equal readiness by noting the increase in the activity coefficients above unity in Table III on proceeding to lower temperatures.

This positive deviation of the results from Raoult's law is contrary to that found for the free energy of dilution of lead chloride by zinc chloride investigated by Wachter and Hildebrand,[5] where a marked negative deviation was found. Their observed results at 500° are shown in Fig. 2 by curve E. If an explanation of the deviation of a_1 from N_1 is sought in the difference of dissociation of the zinc and lead salts, it is found that it leads in the correct direction for lead chloride, but in the wrong direction for lead bromide. Positive deviations from Raoult's law are frequently accompanied by an expansion on mixing, and vice versa, since a respective weakening and strengthening of the internal forces might be expected. Such an explanation would seem plausible in accounting for the negative deviation found for lead chloride where contraction on mixing zinc and lead chlorides amounting to a little over one per cent. was found. However, such an explanation is not applicable to this system where a positive deviation is shown by lead bromide at 400° in spite of almost a two per cent. contraction on mixing. The very much better agreement of this salt with Raoult's law at 500° indicates that the partial molal entropy differs from that of an ideal solution, indicating that the randomness of the arrangement in the solutions differs at the two temperatures. A more searching treatment of this system will be attempted later when data for other systems now being investigated will be at hand.

By graphical integration of the equation given by the Duhem relationship

$$\log a_2/N_2 = -\int_0^{N_2} N_1/N_2 \, d \log a_1/N_1$$

the activities, a_2, and activity coefficients, γ, of zinc bromide in the solutions have been obtained. In performing this integration the difficulty is encountered that N_1/N_2 rapidly approaches infinity as $\log a_1/N_1$ approaches zero. This will not, however, produce any change in the ratio between two values of a_2/N_2 regardless of what method of extrapolation may be chosen. It thus becomes more convenient to evaluate the activity of the solute by choosing the standard state of zinc bromide as the pure salt, rather than the customary state of infinite dilution. With the aid of the equation $\bar{F}_2 = RT \ln a_2$ the partial molal free energy of zinc bromide also was obtained. These values when added to the free energy of formation of

(5) Wachter and Hildebrand, THIS JOURNAL, **52**, 4655 (1930).

zinc bromide from molten zinc and bromine vapor, $\Delta F_2°$, given above, yield ΔF_2. These values are given in Table IV, while Fig. **3** shows the activities of lead bromide and zinc bromide at 400° plotted against their mole fractions.

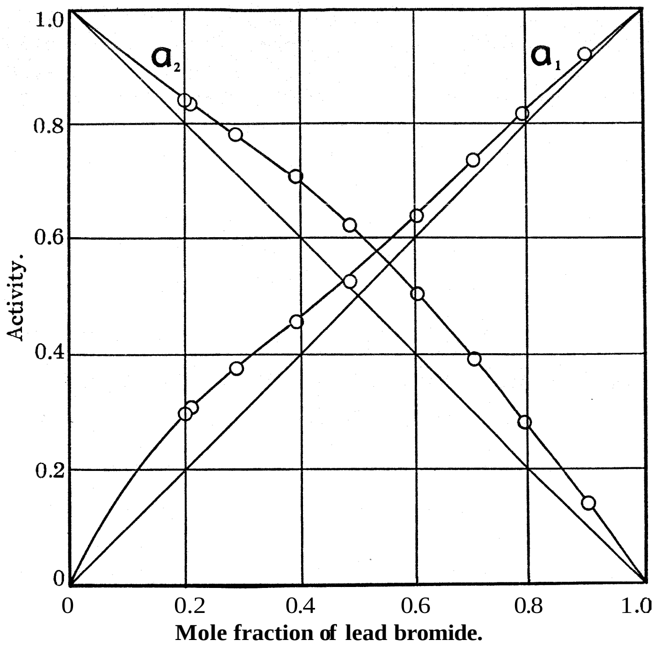

Fig. 3.—Relation of the activities of lead bromide and zinc bromide to their compositions at 400°.

TABLE IV

THERMODYNAMIC PROPERTIES OF ZINC BROMIDE IN THE SOLUTIONS

N_2	a_2	γ	$\bar{F}_2$	ΔF_2	N_2	*at*	γ	$\bar{F}_2$	ΔF_2
		At 400°C.					At 500°C.		
1.000	1.000	1.00	0	—61760	1.000	1.000	1.00	0	—58620
0.800	0.852	1.06	− 210	—61970	0.800	0.812	1.01	− 320	—58940
.790	.844	1.07	− 230	—61990	.790	.803	1.02	− 340	—58960
.712	.792	1.11	− 310	—62070	.712	.730	1.03	− 480	—59100
.608	.717	1.18	− 440	—62200	.608	.637	1.05	− 690	—59310
.514	.630	1.23	− 620	—62380	.514	.564	1.10	− 880	—59500
.396	.509	1.29	− 900	—62660	.396	.443	1.12	—1250	—59870
.296	.397	1.34	—1240	—63000	.296	.331	1.12	—1700	—60320
.206	.283	1.38	—1690	—63450	.206	.230	1.12	—2260	—60880
.098	.140	1.43	—2630	—64390	.098	.110	1.12	—3390	—62010

Summary

E. m. f. measurements of the cells, Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), Br_2(g.), have been made at mole fractions of lead bromide varying between 1.00 and 0.20 at temperatures from 390 to 520°.

Calculations have been made of the activities, activity coefficients, free energies of formation, and partial molal free energies of lead and zinc bromides.

Density measurements have been made upon zinc bromide and a fifty mole per cent. solution of zinc bromide and lead bromide which may be expressed by the equations: $d^t = 3.776 - 0.000913t$ for the salt, and $d^t = 5.086 - 0.001248t$ for the solution.

The positive deviation of the results from Raoult's law has been briefly discussed.

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The Photochemical Polymerization of Methylacetylene and Allene

BY S. C. LIND AND ROBERT LIVINGSTON

The photochemical polymerization of acetylene has been studied quantitatively by Lind and Livingston,[1] who compared the quantum yield with the ion pair yield[2] of the radiochemical reaction. The radiochemical work has been extended by Heisig[3] to include the polymerization of a number of the simpler unsaturated hydrocarbons. The following deals with the photochemical polymerization of two of the compounds studied by Heisig, methylacetylene and its double-bonded isomer, allene.

Rate of Polymerization as a Function of Pressure

Apparatus.—In these experiments a hot mercury arc was used, and particular care was taken to prevent the contamination of the reactants by mercury vapor. The details of the reaction system and the method of operation are described in an earlier paper.[4]

The gases used were highly purified samples,[3] kindly furnished by Dr. G. B. Heisig. They were further purified by low temperature distillation before use.

Reaction Products.—All of the gases studied (except ethylene) were polymerized by the action of ultraviolet light to solid (or viscous liquid) products of low vapor pressure.

The allene polymer precipitated on the walls as a smooth white film, which was either a solid or a very viscous liquid. In one experiment allene at 685 mm. pressure was radiated until the pressure had been reduced by 15.5 mm. The remaining allene was then frozen in a side tube with the aid of liquid air, and the residual pressure was found to be less than 0.2 mm. (the limit of accuracy of the manometer). This may be taken as evidence that the reaction consists of simple polymerization and that not more than 1% of the reaction involves the formation of hydrogen or methane. The polymer apparently has a higher vapor pressure than cuprene, since it can be sublimed in high vacuum by heating the reaction vessel with a direct flame (probably between 200 and

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(1) Lind and Livingston, THIS JOURNAL, 64, 94 (1932).

(2) Lind and Bardwell, *ibid.*, 48, 1556 (1926); Mund and Koch, J. Phys. Chem., 30, 292 (1926).

(3) Heisig, THIS JOURNAL, 53, 3246 (1931).

(4) Ref. 1, pp. 95–96 and Fig. 1.

300°). In one experiment about 90% of the polymer produced from 15.5 mm. of allene was sublimed rapidly in vacuum to one end of the reaction flask. The sublimate was yellowish in color, and, after cooling, it was found that the pressure had been increased from less than 0.2 mm. to 4.5 mm.; approximately one mole of gas was formed by heating the polymer for each three moles of allene polymerized. In another experiment 13.2 mm. of allene was polymerized, and the remaining gas pumped off. A vessel connected to the reaction system by a stopcock was filled with oxygen at a pressure of 30.0 cm. This gas was allowed to distribute itself between the vessel and the evacuated reaction system; the resulting pressure was 146.9 mm. The stopcock was closed and the pressure was observed for forty-five minutes During that time there was no detectable change in pressure. To make sure that no oxygen had been absorbed instantaneously, the reaction system was again evacuated and the side vessel filled to the same pressure as before. The gas was allowed to distribute itself as before; the final pressure was 147.2 mm. These experiments demonstrate that if there is any reaction between the allene polymer and oxygen it is slow at room temperature.

Methylacetylene polymerized to a white substance, which appeared to be a solid. Tests for a permanent gas (methane or hydrogen) gave negative results.

Isoprene was used in a few experiments. It likewise formed a white film when irradiated by a hot mercury arc. The polymer (or condensate) of isoprene burned in air readily and was sublimed in vacuum by heating with a direct flame. The polymerization (or condensation) of isoprene was too slow,[5] to permit the accumulation of a quantity of the reaction product sufficient for other tests.

Although ethylene was not studied quantitatively it may be worth while to report at this time the results of certain qualitative experiments on its photochemical decomposition. In agreement with the results of Bates and Taylor and of Olson and Meyers,[6] we were unable to obtain any indication of reaction when ethylene, at room temperature, was exposed to the complete radiation of a hot quartz mercury arc. However, when ethylene at 27° and at a pressure of 75 cm. was exposed, in a fused quartz vessel, to the radiation from a hydrogen arc (operating at 0.2 ampere), for one hundred and fifty minutes, the pressure decreased by 2.9 mm. and a faint white film was deposited on the walls of the reaction vessel. This film sublimed (or distilled) in vacuum when heated with a free flame. The irradiated gas was tested for acetylene with ammoniacal cuprous chloride, and gave the characteristic red precipitate. The same reagent indicated that the original ethylene contained no detectable quantity of acetylene. The observed formation of acetylene is in agreement with the results of Mooney and Ludlam,[7] who obtained acetylene when they exposed ethylene, in a flow system, to the radiation from an aluminum spark.

Effect of Pressure.—Several experiments were performed at pressures ranging from 3.5 to 68.5 mm. but under conditions which were otherwise similar. These experiments are summarized in Table I. The values of the initial pressures are given in the second

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(5) It is possible that isoprene may undergo a more rapid photochemical reaction which does not involve a change in pressure or the formation of a solid or non-volatile liquid.

(6) (a) Bates and Taylor, THIS JOURNAL, 49, 2458 (1927); (b) Olson and Meyers, *ibid.*, 48, 389 (1926); (c) see, however, Berthelot and Gaudechon, *Compt. rend.*, 159,1169 (1910).

(7) Mooney and Ludlam, *Trans. Faraday Soc.*, 25, 442 (1929). These authors suggest that the formation of acetylene is due to the reaction

$$C_2H_4 + h\nu \longrightarrow C_2H_2 + 2H$$

The following mechanism seems somewhat more probable, and is consistent with the formation of compounds of higher molecular weight (which action was indicated by the precipitation of the film and the decrease in pressure).

$$\begin{aligned} C_2H_4 + h\nu &\longrightarrow C_2H_3 + H \\ C_2H_3 + H &\longrightarrow C_2H_2 + H_2 \\ C_2H_3 + C_2H_4 &\longrightarrow C_4H_6 + H, \text{ etc.} \end{aligned}$$

column The average temperatures are given in the third column. Since the temperature coefficients of these reactions were not determined, no attempt has been made to reduce the measurements to a single temperature. The observed values of the initial rate, in centimeters per minute, are given in the last column To eliminate uncertainties introduced by the absorption of light by the film of polymer, the values of the initial rate are based upon the first 2 mm. change in pressure (except where the total change was less than this amount).

TABLE I

RATE OF POLYMERIZATION OF ALLENE

No.	P_0, cm.	t, °C.	V, cm./min.
1	68.5	10.5	0.029
2	36.5	9.0	.024
3	28.8	10.5	.027
4	26.9	11.6	.024
5	8.3	9.2	.017
6	3.6	9.0	.0115
	Rate of Polymerization of Methylacetylene		
7	35.3	18.8	0.0120
8	20.0	20.9	.0085
9	7.0	22.1	.0060
10	3.7	18.0	.0068
11	3.6	19.1	.0082
	Rate of Polymerization of Isoprene		
12	19.0	29.2	0.0021
13	11.8	26.2	.0016

To illustrate the type of pressure–time curves obtained, the detailed results of several experiments from Table I are plotted in Fig. 1. The numbers attached to the curves are the experiment numbers listed in the first column of the table. Since the temperature of the flowing water-bath sometimes varied by as much as 1.5°, it was necessary to correct the observed pressures to a constant (average) temperature, by means of the perfect gas laws. The volume of the quartz spiral manometer and the capillary connections was sufficiently small to render the effect of fluctuations in room temperature negligible.

The data of Table I are plotted in Fig. 2; the data of Table I, Ref. 1, on the polymerization of acetylene, are also represented on the plot. The form of these rate–pressure curves suggests strongly that the only effect of pressure is to change the percentage absorption and that the rate is directly proportional to the intensity of the absorbed light This conclusion may be tested more definitely by combining the data of Table I with the results of absorption measurements (which are presented in Fig. 4). If the distribution of the energy of the absorbable light produced by the optical system used in the absorption measurements is the same as that from the horizontal arc used in the rate measurements, the assumption that the rate is directly proportional to the intensity of the absorbed light but is otherwise independent of the pressure, leads directly to the following relation[8]

$$V = k(I_{\text{abs}}/I_0)$$

where V is the rate, k is a factor which is a constant for each gas, and (I_{abs}/I_0) is the ratio of the intensity of the absorbed light to that of the incident light, in the absorption measurements. In Fig. 2, $k(I_{\text{abs.}}/I_0)$ is represented ***by*** a solid line, which (by adjusting k) has been made to coincide with the average value of V at a pressure of 30 cm. The agreement between the slopes of the dotted and solid lines is, in each case, close enough to afford strong support for the correctness of the assumption. The small departures may be due either to experimental error or to a difference in the energy distributions of the two sources.

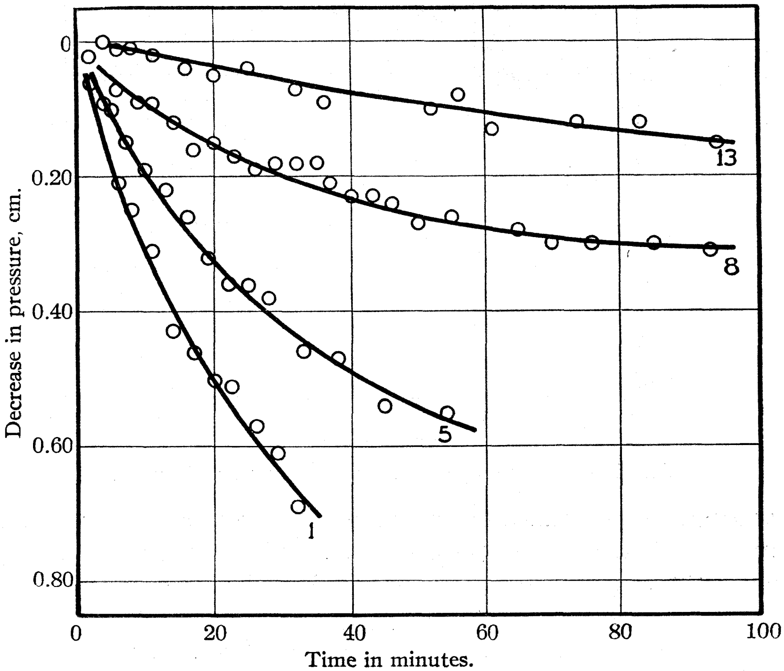

Fig. 1.—Rate of polymerization.

Determination of the Quantum Yield.—The apparatus used in these measurements was similar to that used in the determination of the quantum yield of the polymerization of acetylene, and has been described by Lind and Livingston.[9]

A few minor adjustments of the focal isolation monochromator were made in an attempt to reduce the amount of stray light of longer wave

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(8) See Ref. 1, p. 98.

(9) Ref. 1, pp. 100-103.

length, but the character of the light source was essentially the same as that used in the earlier measurements.

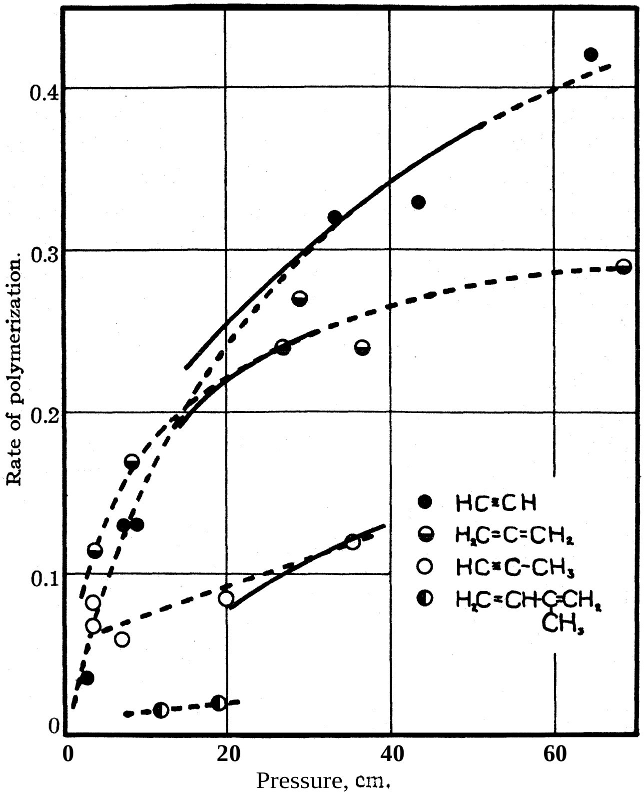

Fig. 2.—Rate of polymerization as a function of pressure.

The energy measurements were made with the same galvanometer and thermopile. The results of the calibrations, which were made during the course of the experiments, are summarized in Table II.

TABLE II

CALIBRATION OF THE THERMOPILE AND GALVANOMETER

Amperes through filament[a]	Ergs/ sq. mm. sec.[b]	Average deflection, mm.	Ergs/sq. mm. sec. per mm. deflection
0.250	4.26	264	0.01614
.300	6.27	390	.01609
.350	8.67	532	.01611

[a] The current was measured with an accurate ammeter kindly furnished by the Department of Electrical Engineering of the University of Minnesota.

[b] Calibration of the Bureau of Standards for flux at two meters distance from the standard lamp.

When proper allowance is made for the shunt (which was used to reduce the sensitivity during the calibrations) and for the area of the thermopile, and corrections are applied for absorption and reflection, both by the fluorite window of the thermopile and the second window of the quartz reaction vessel, the working value of the sensitivity is 3.82 ergs/sec. per mm. deflection.[10]

Except for a few minor improvements in the electrical circuit the differential manometer was identical with that used in the earlier measurements. To reduce the effect of temperature fluctuations the reaction vessel and manometer were enclosed in a small box, which in turn was placed in a large air thermostat. No attempt was made to regulate the temperature during the experiments with allene, the thermostat consisting simply of a large box containing a small electric fan. While the temperature was approximately constant during each experiment, the several experiments were performed at temperatures ranging from 25 to 29°. During the experiments with methylacetylene a simple, electrically shielded thermoregulator was used, which kept the temperature at 25°. The differential manometer was compared, before and during the progress of the experiments, to an accurately calibrated McLeod gage, at pressures ranging from 0.7 to 0.1 mm. All of these results fitted the following semi-empirical equation within 1 or 2%.

$$\Delta P(\text{mm.}) = 3.23 \times 10^3 \frac{\Delta C}{C_2^2 \cdot C_1} \quad {}^{11}$$

where C_1 and C_2 are, respectively, the initial and final readings of the variable condenser.

To determine the number of quanta corresponding to the energy absorbed, it is necessary to know the average wave length of the absorbed light. This was determined approximately by comparing a spectrogram of the light emerging from the focal isolation apparatus with absorption spectrograms of allene and methylacetylene.[12] A hydrogen arc, operating at 3000 volts and 0.3 ampere, was used as a source of light. The cell used in the absorption measurements was 10 cm. long, was of fused quartz, and was provided with plane ends Oiled process plates were used.

The following results were obtained with a small quartz spectrograph. At room temperature and at 60 cm. pressure allene completely absorbed

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(10) The correction for reflection and absorption is probably uncertain by about 10%. It seems quite probable that the value, 4.40 ergs/sec. per mm., of the sensitivity used in the acetylene measurements is too high and that a better value would be 4.00 ergs/sec. per mm. This change would increase the average value of the quantum yield for acetylene polymerization from 9.2 to 10.1, but would not affect any conclusions which have been presented.

(11) Due to a misprint, the constant of the corresponding equation of Ref. 1, p. 102, reads 10^4 instead of 10^3.

(12) Absorption spectrograms of vinylacetylene were also taken, although rate measurements were not made with this gas. At 35 cm. pressure absorption was complete at 2480 Å. and appreciable at 2540 Å. When a side tube was immersed in a solid carbon dioxide–acetone bath [see Nieuwland. Calcott, Downing and Carter, THIS JOURNAL, 53, 4200 (1931) for vapor pressure data] the absorption was complete at 2280 and was still appreciable at 2400 Å. The absorption was definitely banded. The sample of vinylacetylene used in these experiments was prepared from a solution of pure vinylacetylene in toluene, kindly furnished by Dr. H. W. Ellry, Director of the Chemical Section, E. I. du Pont de Nemours and Company.

light of wave length shorter than 2340 Å. and showed some absorption to 2380 Å. At a pressure of 12.5 cm. the absorption was complete at 2290 Å. and was appreciable at 2370 Å. Methylacetylene at a pressure of 44 cm. showed complete absorption at 2190 Å. and appreciable absorption at 2240 Å. We have, somewhat arbitrarily, taken the average wave length of the light absorbed in the quantum yield experiments as 2200 Å. for methylacetylene and 2300 Å. for allene. The value of the energy of a quantum based on these estimates is not likely to be in error by as much as 5%.

After the completion of the rate and quantum yield measurements, a Steinheil spectrograph with two quartz prisms became available for our use. This instrument was adjusted for minimum deviation of λ 2200 Å. An iron arc was used as a reference spectrum.

Absorption spectrograms of acetylene were taken at a pressure of 45 cm., with a side tube immersed in a mixture of solid carbon dioxide and acetone. A series of sharply defined bands were obtained between 2230 and 2100 Å. These bands occur between the regions photographed by Herzberg[13] and by Kistiakowsky.[14] This is in agreement with the fact that the pressure of acetylene was intermediate to the pressures used by these investigators. Since the absorption of the fused quartz cell used in these experiments set in at about 2100 Å. it was impossible to observe bands at shorter wave lengths or to determine whether any continuous absorption was present.

No banded structure could be detected in the spectra of either allene or methylacetylene. The apparent transmission limits, while varying somewhat with the time of exposure, are in agreement with those determined with the small spectrograph. Allene was photographed at a pressure of 51 cm. and also with a side tube immersed in a mixture of solid carbon dioxide and acetone (corresponding to a pressure of about 6 cm.). The limit of transmission was about 2330 Å. for the higher pressure, about 2200 Å. for the lower. Methylacetylene was photographed at 44 cm. pressure. Cooling the side tube to −23°, which is above the boiling point of methylacetylene, had no effect whatever on its absorption spectra.

These results throw some doubt on the interpretation of the quantum yield measurements for allene and methylacetylene. The existence of a continuous absorption for allene and methylacetylene would not have been predicted, and the observation of a continuous (or quasi-continuous) absorption suggests that the observed absorption may be due to the presence of (less volatile) impurities. However, the following facts may be cited as evidence against the hypothesis that the continuous absorption is due to impurities. 1. The gases were very carefully prepared and purified[8] and neither vapor pressure measurements[15] nor molecular weight

(13) Herzberg, *Trans. Faraday Soc.*, 17, 378 (1931).

(14) Kistiakowsky, *Phys. Rev.*, 37, 276 (1931).

(15) Livingston and Heisig, This Journal, 52, 2409 (1930); also Heisig, unpublished work.

determinations gave any indication of the presence of impurities. 2. An impurity if present was apparently not light sensitive, since there was no change in rate of polymerization during the course of an exposure (other than that observed in the preliminary experiments due to the formation of an opaque film of polymer on the window.) **3.** The products of polymerization of the two compounds were apparently identical, and there was never (in either preliminary or final measurement) any detectable quantity of bromine formed.[16] 4. The observed absorption limits and the total absorption of methylacetylene and acetylene differ by only 10%. 5. Immersing a side tube of the absorption cell in a low temperature bath did not affect the absorption spectra of methylacetylene at all, and only shifted the absorption limit of allene to an extent comparable with its reduction in pressure.

The answers to the questions raised here must await the development of new methods of preparation of these gases or of more certain methods for their purification. A comparison of the ion pair and quantum yields of acetylene with those of methylacetylene and allene indicates that if an impurity were present (in the latter two) and if it had any effect on the results, it must have been acting as an internal filter, not as a sensitizing agent.

The procedure followed and the precautions observed in the final series of rate measurements were similar to those discussed by Lind and Livingston.[17] To illustrate the type of pressure variations obtained, the detailed

TABLE III

DETERMINATION OF THE QUANTUM YIELD OF ALLENE

No.	P, mm.	Δp, mm.	t, min.	Ergs/sec. absorbed	Quanta absorbed $\times 10^{-17}$	Molecules reacted $\times 10^{-17}$	M/Q
1	316	0.270	33	980	2.25	6.4	2.8
2	313	.380	60	935	3.9	9.0	2.3
3	285	.481	50	990	3.5	11.3	3.2
4	216	.305	60	830	3.5	7.2	2.1
5	209	.294	50	775	2.7	6.9	2.6
6	204	.278	60	830	3.5	6.6	1.9
						Average	2.5
		Determination of the Quantum Yield of Methylacetylene					
7	386	0.131	60	245	0.99	3.35	3.4
8	371	.141	100	150	1.03	3.6	3.5
9	371	.096	100	140	0.92	2.5	2.7
10	233	.130	72	175	.84	3.3	3.9
11	162	.129	70	175	.82	3.3	4.0
						Average	3.5

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[16] The method of preparation of allene (3) would suggest that the most probable impurity would be dibromopropene. It should be noted, however, that a halide was not used in the preparation of methylacetylene.

[17] Ref. 1, pp. 104–105.

results of several experiments are plotted in Fig. 3. The readings of the variable condenser are plotted against time in minutes. The numbers on the curves are the experiment numbers of Table III.

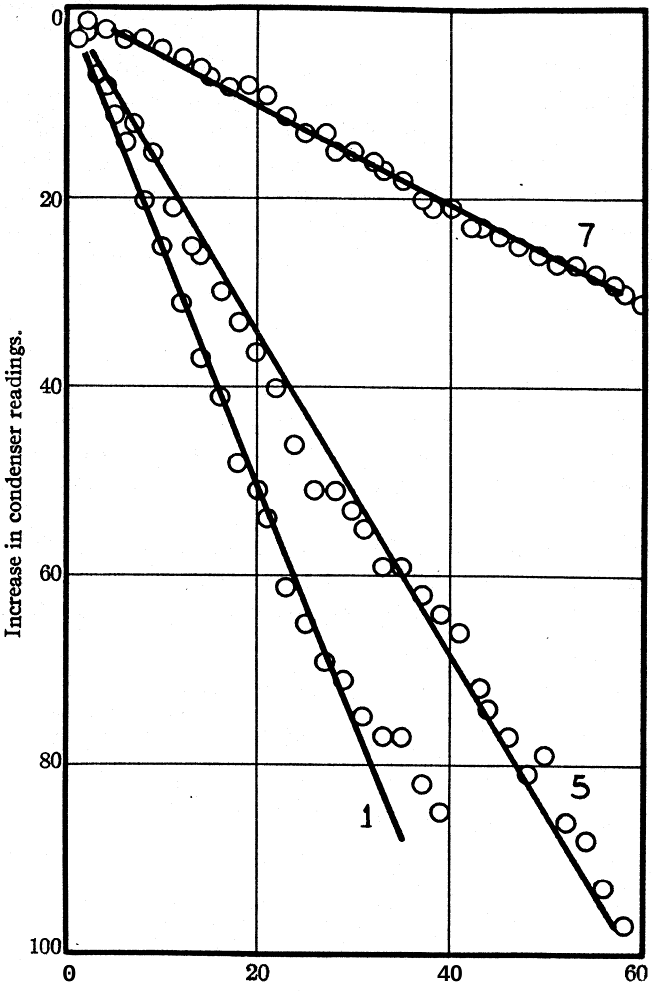

Fig. 3.—Rate of polymerization.

The percentage absorption of light by allene and by methylacetylene, in the reaction vessel and at the pressures used in the rate measurements, was determined in separate series of measurements. These experiments are summarized in Fig. 4. The percentage of the transmitted light absorbed is plotted against the pressure of the gas. The corresponding results for **acetylene**[18] are also represented in this figure. It is interesting to note that

[18] Ref. 1. Fig. 6.

both in the total absorption of the light from the focal isolation apparatus, and in the limits of absorption indicated by the spectrograms, methylacetylene is similar to the structurally related acetylene, but differs widely from its (double-bonded) isomer, allene.

The results of six determinations of the quantum yield of the polymerization of allene and five of that of methylacetylene are summarized in Table III.

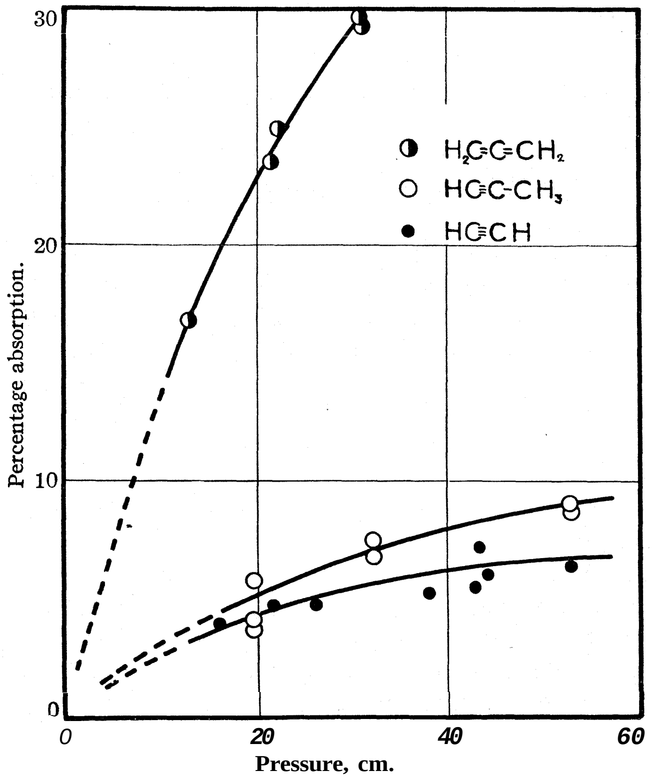

Fig. 4.—Absorption as a function of pressure.

The pressures listed in column two are the initial pressures of the reacting gas. The total change in pressure in millimeters is given in column three, and the corresponding decrease in number of gas molecules (X 10^{-17}) is given in column seven. The duration of the experiments in minutes is given in column four. The average energy of the absorbed light in ergs per second is given in column five. These values are based upon measurements of the energy of the transmitted light, made at fifteen-minute intervals during the course of each experiment, and upon the percentage absorption data recorded in Fig. 4. The total number of quanta absorbed (X 10^{-17}) is given in column six. The quantum yield is given in the last column.

It is apparent that, within the limits of experimental error, the quantum yield is not dependent either upon the pressure of the gas or upon the intensity of the absorbed light.

In Table IV the average values of the quantum yields are compared to the ion pair yields for the four polymerization reactions which have been studied, with both forms of activation. The formula of the gas polymerized is given in the first column. The quantity listed in the last column is the ratio of the ion pair yield to the quantum yield.

TABLE IV

COMPARISON OF ION PAIR YIELD TO QUANTUM YIELD FOR POLYMERIZATION REACTIONS

Gas polymerized	M/N	M/Q	$(M/N)/(M/Q)$
$HC{\equiv}CH$	18[3]	10.1[19]	1.8
$HC{\equiv}CCH_3$	8.3[3]	3.5	2.4
$H_2C{=}C{=}CH_2$	10.4[3]	2.5	4.2
$(CN)_2$	7.4[20]	3[21]	2.5

The only regularity which is apparent from these data is that the quantum yield is never greater than the ion pair yield. This same relation has been found to hold for all other reactions which have been studied both radiochemically and photochemically. It would not be justifiable to place too much emphasis on the exact value of the ratio $(M/N)/(M/Q)$. It is difficult to estimate the probable error of the absolute value of M/N, but it is probably about 10%. Due to possible uncertainties in the energy measurements,[21] the probable error of the absolute value of M/Q may be as great as 20 or 30%. In addition to the uncertainty in the values of the ratios, it must be remembered that in the cases of allene and methylacetylene the products of reaction are apparently different for the photo and radiochemical reactions. It is also quite probable that the values of the ratio are functions of temperature. The effect of temperature has been studied only in the case of acetylene, but in that case the ion pair yield is independent of temperature, from 0 to 100°,[2] while the photochemical reaction has a ten degree temperature coefficient of 1.25.[22]

While this paper was in proof, it came to our attention that Berthelot ("Notice sur les travaux scientifiques de M. Daniel Berthelot," Paris, 1917, p. 130) had previously reported that methylacetylene polymerizecl under the influence of light to a white solid. This reference is quoted by Dahr ("The Chemical Action of Light," London, 1931, p. 303); we have not yet obtained access to the original.

In conclusion we wish to express our appreciation of-the assistance of Savetta L. Livingston in the performance of the quantum yield measure-

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(19) Lind, Bardwell *and* Perry, THIS JOURNAL, 48, *1556 (1926).*

(20) Hogness and Liu-Sheng Ts'ai, *ibid.*, **54,** *123 (1932).*

(21) *See* Leighton, *J.* Phys. *Chem.*, 36, 1882 *(1932).*

(22) Ref. **1,** pp. *98–99.*

ments, and of Henry M. Davis and Dr. George Glockler in the adjustment of the Steinheil spectrograph.

Summary

1. Both allene and methylacetylene are polymerized to white solids when they are exposed (separately) to ultraviolet light.

2. The results of Mooney and Ludlam on the photolysis of ethylene have been confirmed.

3. Qualitative determinations of the long wave length limit of absorption for allene, methylacetylene and vinylacetylene have been made.

4. The quantum yield for the polymerization of allene is 2.5; for methylacetylene, 3.5. For both reactions the quantum yield is independent of the pressure and of the intensity of the absorbed light.

5. A comparison of quantum yields to ion pair yields has been made for four polymerization reactions.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

Extra Specific Heat in Cuprous Sulfide; Specific Heat of Ferrous Oxide

BY WALTER P. WHITE

Determinations of the specific heat of cuprous sulfide up to 900° have shown a region of abnormally high specific heat at 300° and above, where there is no corresponding crystallographic change of state, Since such variations in specific heat are of recent discovery and are now being studied in various substances, it seems desirable to publish the data. Along with them are given two specific heats of ferrous oxide, determined, apparently, for the first time.

Method and Apparatus

The method is the "dropping" method, with a water calorimeter. The furnace was practically the same as reported on in 1921,[1] platinum wound on a thin-walled alundum tube of 28 mm. inner diameter, and 30 cm. high. At that time there were vertical gradients of 30° in 12 cm, at 900° and a difference of 8° between the specimen and the thermocouple junction immediately beside it. In the present case similar differences were reduced to 2°

The chief agent in this improvement was a separately heated plug in the furnace bottom, which was disconnected just before being dropped out to make way for the specimen. Since the maximum temperature was only 900° this plug could be more easily made and preserved than in some previous work, where 1400° was reached. A description of this plug will be published elsewhere.

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(1) Latent heats of melting of nickel and monel metal, White. *Chem. Met. Eng.*, **25**, 17 (1921).

Tests made on another furnace, where a heavy silver tube gave great uniformity of *wall* temperature, had given strong indication that irregularity of temperature was produced in the furnace cavity by conduction of cold down the mullite insulating and supporting tubes. Hence the specimen was supported from below on a small shelf, and was inside a heavy sheet gold cylinder (0.4 mm. thick) closed entirely at the top save for a small hole to admit the platinum thermocouple and its two slender insulating capillary tubes. A Marquardt tube 6 mm. in diameter passing down outside the cylinder acted as a shaft to hold the shelf, and turn it aside in making the drop.

Although the high conducting power of the gold undoubtedly helped to equalize temperature, conduction alone can easily be shown to be of limited value for structures of any size. But the high reflecting power of the surface must have equalized the radiation within the cylinder, and thus diminished the difference of temperature between the specimen and the thermocouple beside it.

A special difficulty arose through the necessity of protecting the specimens from the air. The only trustworthy way to do this appeared at the time to be by inclusion in silica glass tubes. Since these had to be drawn down and sealed after the specimens were in them they had to be rather small, and were actually 1.3 cm. in diameter. As a result the total heat capacity of cuprous sulfide and container averaged over 2.5 times as much as that of the specimen alone, and the accidental error of each final result was therefore around 2.5 times that of the determination which gave it. The ratio for FeO was only a little more favorable.

The heat loss in dropping the specimen, and also much of the systematic error of the temperature distribution in the container, was canceled by the method of the best experimenters, namely, dropping a blank container. The container results at 400 and 700° were obtained by interpolation on a curve derived from the other four results and also from the curve for silica glass published in 1919.

The comparison, summarized in Table I, shows a very significant difference between the older and the newer values. The increase in the mean specific heat of silica glass from the interval 0–300° to the interval 0–900° appears to be 0.0008, or 0.35%, greater by the later determinations, although the heat loss in dropping, which affects the later but not the earlier results, must have lowered the values for higher temperatures more than those for lower. This discrepancy calls for investigation as soon as a suitable furnace is ready. It cannot be due to greater radiation from the furnace to the calorimeter at 900°, for successful and consistent special measurements showed that such radiation caused less than 0.0001° rise. Until this discrepancy is explained we cannot tell whether it makes the low-temperature results for cuprous sulfide too high or too low. If it is due to a difference in the two kinds of silica used, as seems quite possible, of course it causes no error at all. But in any case the resulting error would be only one-sixth of the abnormal difference between the cuprous sulfide specific heats for the two lower intervals, hence it does not shake the evidence for the existence of a real abnormality.

The error from vaporization and splashing as the specimen strikes the water in the calorimeter was completely eliminated by a combination of two excellent devices each of which had previously been used alone by others. These were Plato's narrow cup, knocked under the surface of the water by the specimen falling into it, and a spring shutter, closing the calorimeter top.

In 1920, with temperatures of 1270° and above, each of the "silky" silica inclosures, with one exception, cracked the first time it was dropped into the water. The crack was heard about a minute after the drop, and hence was presumably due to cristobalite formation, which would be effective when the cristobalite inversion temperature, about 180°, was reached in cooling. In the present case all three inclosures, of clear silica, are still intact, though slightly opaque on the surface. That for the cuprous sulfide, after 18 drops, has lost 27 mg. out of 8.18 g. The other two have lost no perceptible weight.

In order to prevent the specimens, which were in small lumps, from packing and splitting the inclosures, they were put in cases of thin sheet metal, copper for the cuprous sulfide, and platinum for the ferrous oxide.

Materials

The cuprous sulfide was a sample of natural mineral which had been analyzed for some previous work.[2] The analysis gave: Cu, 78.68; S, 20.32; Fe, as pyrite, 0.69; SiO_2, none; total 99.78; ratio of Cu to S, 2.032:1. When heated in the unsealed silica tube in a hydrogen atmosphere it lost 22 mg. in about 8.5 g. It is probable that a little of the loss was moisture, but most was sulfur, from the pyrite impurity. The correction for remaining impurities is probably a little under 2 per mille, and negative. On the other hand, the excess copper in the Cu_2S increases the mean atomic weight of it 0.00207 times. If we assume that the mean atomic heat is the same for this mixture as for the pure compound, an assumption surely good to 20% of the small difference involved, the specific heat of the actual mixture is below that of the pure compound by 2 per mille, which almost exactly offsets the other correction, so that the specific heat of the total mass dropped may be taken to be, well within the experimental error, the same as that of the pure material.

The ferrous oxide was some of the material made at the Fixed Nitrogen Research Laboratory for R. W. G. Wyckoff's work on its x-ray structure. The only impurity is magnetite. Dr. H. E. Merwin kindly selected superior lumps by use of an electromagnet, and analyzed them under the microscope. The impurity is about 6%. An approximate correction for this single impurity is given below.

Below 570° FeO is unstable. In order to avoid the effects of the slow transformation which takes place at temperatures somewhat below that, the specimen was put into the hot furnace, rising above 600° in about six minutes.

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(2) The sulfides of copper, Posnjak, Allen and Merwin, *Econ. Geol.*, 10, 508 (1915).

TABLE I

BLANK INCLOSURE OF SILICA, WEIGHT 8.164 G.

Serial number of experiment	23	25	19	21[a]	9	10	8	15
Furnace temp., U°	299.8	299.9	500.3		601.2	601.2	900.7	900.1
Final temp., L°	29.7	29.9	29.9		30.2	30.0	29.5	30.1
Total calories	475.70	475.04	893.14		1115.4	1117.4	1804.7	1802.5
Cal. per gram	58.268	58.188	109.40		136.62	136.87	221.06	220.79
Cal. 0°–L° (calcd.)	5.125	5.160	5.16		5.21	5.18	5.09	5.19
Cal. 0°–U°	63.393	63.348	114.56		141.83	142.05	226.15	225.98
Interval heat	0.21145	0.21123	0.22898		0.23591	0.23628	0.25108	0.25106
Interval heat of silica glass 1919	0.21245		0.23025		0.23666		0.2512	

[a] This determination had a slight mishap. Result omitted.

TABLE III

ABRIDGED, CUPROUS SULFIDE, 30–300°, 400°, 500°, 600°, 900°

Serial number	6	7	24	17	26	16	22	1	2	5	20	3	4
Furnace temp.	300.5	300.4	299.9	399.7	400.3	501.2	500.4	[a]	600.4	601.1	599.4	900.1	899.4
Lower temp.	29.4	29.8	29.8	29.7	29.9	29.5	29.6		29.9	30.1	29.6	30.3	30.2
Total cal.	871.9	869.0	865.1	1256.1	1258.2	1610.2	1606.0		1964.2	1963.4	1955.3	3047.4	3044.0
Total per g. Cu_2S, even intervals	43.66	43.49	43.36	58.35	58.56	71.61	71.69		84.75	84.73	84.39	122.4	122.2
Mean		43.60		58.46		71.64				84.62		122.3	

[a] Result omitted; 11 calories low, or 5.7 per mille. Cause not apparent.

TABLE II

CUPROUS SULFIDE, 30–700°, 8.533 G. Cu_2S

Serial number of experiment	18	27	28
Furnace temp., U°	700.7	700.8	700.9
Final temp., L°	29.9	29.8	29.7
Total calories	2316.1	2317.0	2316.1
Cals., less Cu	2224.9	2225.8	2224.8
Interval heat of silica, 0°–U°	0.24184	0.24184	0.24184
Total heat of silica per g., 0°–U° (calcd.)	169.70	169.76	169.82
Total heat of silica, 0°–L° (calcd.)	5.16	5.14	5.12
Total heat of silica, L°–U°	161.54	164.62	164.70
Total cal. SiO_2	1399.6	1398.8	1399.0
Total cal. Cu_2S	825.3	827.0	825.8
Cal. per g. Cu_2S, L°–U°	96.69	96.89	96.75
Cal. per g. Cu_2S, 30–700°	96.586	96.760	96.594
Average		96.647	

TABLE IV

FERROUS OXIDE, 30–700°, 900°; 10.1058 G. FeO

Serial number	11	12	13	14
Furnace temp	700.3	700.8	900.7	900.1
Lower temp.	29.8	29.5	29.3	29.5
Total cal.	2779.5	2783.2	3706.8	3704.1
Total per g. FeO even intervals	123.91	123.92	163.22	163.31

The silica glass containers weighed, respectively, 9.1494 g., 8.530 g. and 8.1640 g.

TABLE V

VALUES OF THE HEAT REQUIRED TO RAISE CUPROUS SULFIDE THROUGH SUCCESSIVE INTERVALS

	Calories **per** gram
300–400°	14.96
400–500°	13.19
500–600°	12.98
600–700°	12.02
700–900°	2 × 12.82

Discussion

A consideration of the discrepancies between the individual observations indicates that the decrease from the second to the third value appearing here may not be real, though it probably is, but that the other changes, and especially that from the first to the second value, do actually exist.

Since only two values for FeO were obtained, the most elaborate equation that can be derived for its specific heat is one of two constants.

Taking such an approximation as the only one available, we have the interval specific heat as

$$0.17508 + 0.0000135t$$

and the true specific heat, therefore

$$0.17508 + 0.000027t$$

This equation is evidently most nearly accurate between 700 and 900°. According to it the interval specific heat increases about 1.44% in 200" near those temperatures. Another oxide of a heavy metal which has been determined with considerable accuracy in this region is zinc oxide.[3] Its interval heat increases a little over 2%, from 0.14370 to 0.14661, in the same interval. The equation for it, holding from 700 to 1100°, is approximately $0.13304 + 0.0000158t - 0.0000000008t^2$, which may give some sort of idea of the deviation from linearity to be expected in such specific heats. The mean atomic heat of the zinc oxide at 800° is 6.35, that of the ferrous oxide, 7.1. The well-known atomic heat curves of oxides are of such a character that the higher the atomic heat is, the less rapidly it increases with temperature.[4] Hence the association of the lower mean atomic heat of the zinc oxide with a higher rate of increase of the heat is entirely normal. This relation, however, properly applies when the atomic heat is below the Dulong and Petit value, 5.96. Its appearance, therefore, when the atomic heat is far above that value is of considerable interest. But it can hardly be discussed adequately without more data.

If we assume that the mean atomic heat of magnetite is the same as that of ferrous oxide the specific heat of magnetite is to that of ferrous oxide as 36:33.14, or, nearly enough, as 12:11. Hence the specific heat of the 6% of magnetite impurity is in the ratio of 6 × 12 against 94 × 11 for the ferrous oxide, and the actual total heat is in the ratio of 72 + 1034, or 1106, against 1100 for pure ferrous oxide. Hence 6/1106 or 0.54% may properly be subtracted from all ferrous oxide values given thus far.

Precision, that is, Agreement, of the Results.—Of the twelve different points determined, one-third show a discrepancy corresponding to 0.8° or over of furnace temperature, or 0.003° of calorimeter temperature, and these discrepancies are about as great at low as at high temperatures. At 700° and above the proportional precision is 1 per mille or better, which is about as good as any previous work, even where conditions were much easier. It agrees rather well with the observed inhomogeneities of furnace temperature. The equally large, and proportionally larger, errors at the lower temperatures are puzzling. Some of the causes of error, including those apparently the most serious, such as furnace temperature heterogeneity, must have been much smaller. The few errors which might have had the same size throughout, such as that in finding the final calorimeter temperature, which was about the same in all cases, are shown by systematic tests[5] and careful study to have been almost certainly negligible.

Lag in the distribution of the furnace temperature, which appeared very strikingly indeed in the studies made on the furnace, and which is greater at lower temperatures, appears, partly by a process of exclusion, to be the

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(3) **Day and White,** THIS JOURNAL, **48,** 369 (1926)

(4) **Compare White,** *Am. J. Sci.*, **47,** 22 (1919)

(5) Particularly the kind described in *ibid.*, 47, 7, 53. 54 (1919).

only thing which can reasonably be suggested as a cause of these errors. If that is the chief cause, a repetition made with that point in view should increase the precision somewhat. This, however, would be an unprofitable proceeding; a furnace of different type can be made far more precise at lower temperatures than any practicable furnace of wire and refractories can possibly be. Indeed, all other lower temperature specific heat work in our laboratory has been done with a special furnace;[6] and there was no expectation, when the present work was started, of making observations below 600°. These were undertaken when the first results, at higher temperatures, showed that there was something very peculiar lower down. If further examination of the anomaly in Cu_2S near 300° seems desirable, it should undoubtedly be done with a lower-temperature furnace. Meanwhile the data of chief metallurgical importance, at higher temperatures, for which the work was undertaken, seem quite satisfactory, though the proposed reexamination of the specific heat of silica glass may change them slightly.

Acknowledgment.—Grateful acknowledgment is made to the Phelps Dodge Corporation and to the Carnegie Steel Company, who suggested this work, and contributed liberally to its cost.

Summary

The specific heats of ferrous oxide for the intervals 30–700° and 30–900°, and those of cuprous sulfide for six intervals up to 900°, were determined by the dropping method with various improvements in furnace and calorimeter.

The necessity of inclosing against the air (in silica glass) diminished precision, especially by increasing the amount of dead material and by compelling the thermoelectric thermometer to be outside the sample tested. This about offset the effect of the improvements in apparatus, so that the precision at the higher temperatures only averages the same as in the best previous work.

At the lower temperatures some of the results are not as good.

Over an interval of several hundred degrees, centering somewhere near 300°, there is an excess specific heat in cuprous sulfide of 3 or more calories per gram, similar to those discovered in rhodium near 1300°, in manganese dioxide near 90°K., and in (to date) about a dozen other substances.

WASHINGTON. D. C

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[6] White, *Phys. Rev.*, 31, 681 (1910).

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Arsenic. I. The Analysis of Arsenic Tribromide. II. The Analysis of Arsenic Trichloride

BY GREGORY P. BAXTER, WILLIAM E. SHAEFER, MERRILL J. DORCAS AND EDWARD W. SCRIPTURE, JR.

In a recent determination of the atomic weight of arsenic, Krepelka[1] has found the value 74.934 for this element by analysis of arsenic trichloride. In calculating the result, however, the atomic weight of chlorine is assumed to be 35.458. If the more probable value for chlorine, 35.457, is used, Krepelka's value is raised to 74.938.[2] Aston[3] from results with the mass-spectrograph finds arsenic to be a simple element with the packing fraction -8.8×10^{-4} and the atomic weight 74.934. But this value has not been corrected from the physical scale, $O^{16} = 16.0000$, to the chemical scale. If the conversion factor of Babcock and of Naudé, 1.00012, is used the atomic weight of arsenic becomes 74.927, but with the equally possible one of Mecke and Childs, 1.00022, the atomic weight of arsenic is 74.919. The original exact agreement of Krepelka's and Aston's results thus disappears.

Recent success in the preparation and analysis of volatile inorganic halides in this[4] and other laboratories led us to use similar methods in the case of arsenic. The results of this work were satisfactory so far as can be told and yield an atomic weight of arsenic slightly less than 74.91.

I. The Analysis of Arsenic Tribromide[5]

Two samples of arsenic tribromide were prepared, the first of which served only for preliminary analyses. The method of synthesis from the elements and purification by prolonged fractional distillation in exhausted all glass apparatus resembled closely that used in the investigations cited above.

In the preparation of Sample I, crystals of commercial metallic arsenic were placed in a glass bulb to which were attached two special all-glass valves (D, Figure 1), which could be opened by breaking at will, and the bulb was highly evacuated. In another glass bulb, attached to the first through one of the valves, was placed a slight deficiency of the purest bromine and, after the air had been flushed out of the bulb by boiling the bromine under reduced pressure, the glass tube leading to the pump was sealed. Then the valve between the bulbs was opened and the bromine vapor was allowed to act upon the arsenic at ordinary temperature. Occasional agitation was necessary during this operation in order to avoid accumulation of bromine in the bromide, which remained above the melting point owing to the heat of reaction. The bulb was allowed to stand

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(1) Krepelka, *Coll. trav. Chim. Tchecoslov*, **2**, 255 (1930).

(2) See first report of the International Committee on Atomic Weights for 1930, This Journal, **53**, 1627 (1931).

(3) Aston, *Proc.* Roy. *Soc* (London), **A115**, 505 (1927)

(4) Baxter, Weatherill and Scripture, Proc. Am. *Acad*, *68*, 245 (1923); Baxter and Scott, *ibid.*, **59**, 21 (1923); Baxter and Fertig, This Journal, 46, 1228 (1923); Baxter and Cooper, *Proc. Am Acad.*, 69, 235 (1924); 60,291 (1925); Baxter and Butler, This Journal, 48,3117 (1926): 60,408 (1928).

(5) The purification and analysis of arsenic tribromide was carried out by W E. Shaefer.

for some time until all evidence of uncombined bromine had disappeared. Preparatory to distillation the bulb containing the bromide was connected to a pump through a capillary and the bromide was boiled under reduced pressure to flush out gases, especially hydrogen bromide, before it was permanently sealed.

The bromine had been purified by a standard method used in this Laboratory. consisting in brief of the following steps. two successive distillations from solution in concentrated aqueous potassium bromide, the bromide in the second distillation having been made from a portion of the product of the first distillation; conversion to potassium bromide by means of potassium oxalate and fusion of the product with permanganate to eliminate organic matter; removal of iodine by liberation of a small proportion of the bromine with acid permanganate and boiling; liberation of about 80% of the remaining bromine with pure permanganate and sulfuric acid; drying with phosphorus pentoxide and distillation.

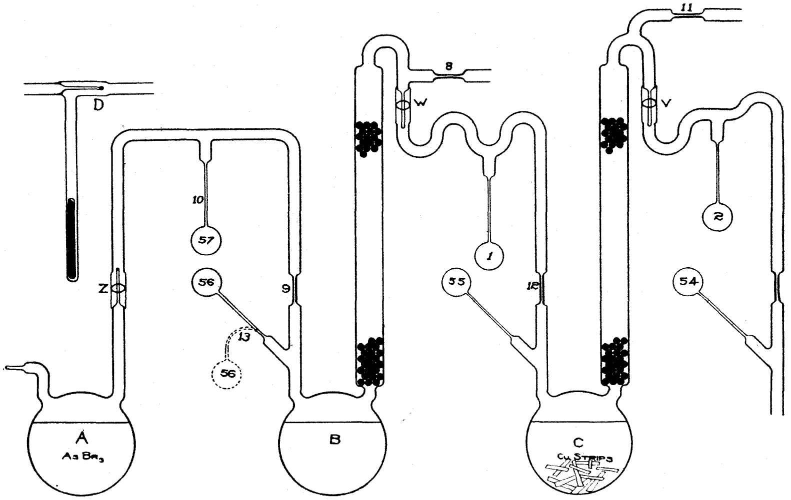

Fig. 1.

The arsenic tribromide was distilled from the excess of arsenic into a second similar bulb connected to the first by a special valve and previously exhausted, and then was fractionally distilled in apparatus resembling that shown in Fig. 1. The Hernpel column attached to the still was filled with glass beads and during the distillation was warmed with a flame sufficiently to prevent choking of the column. In each distillation the more volatile fraction was collected in small bulbs, 1, *2*, beyond the column, while a residual fraction was either left in the still or collected in small attached bulbs, 55, 56. During the tenth distillation the apparatus was broken, and as the quantity of material remaining was small, it was discarded. A diagram of the distillation is shown in Fig. *2* in which the capital letters represent the main portions and numbers to the right represent more volatile and numbers to the left less volatile fractions. The sequence of numbers as a whole represents gradually decreasing volatility so far as any such difference actually existed.

The originally brown tribromide improved rapidly in appearance as the fractionation proceeded. After the first few distillations the liquid substance was pale yellow and the solidified nearly colorless; but even at the end the residue in the still always possessed a dark color. Three only of the head fractions were analyzed with the results indicated on the diagram and in Table I, Series 1.

Sample II was prepared from pure bromine and arsenic in essentially the same manner as Sample I. From the weights of arsenic and bromine used the weight of tribromide synthesized was calculated to be approximately 425 grams. Only minor modifications were made in the construction of the distillation apparatus as shown in Figure 1. The Hempel columns were suitably warmed by electrically heated sleeves.

In spite of the fact that an excess of arsenic was employed in the synthesis the most volatile fraction in the first distillation was red and appeared to contain free bromine Possibly this was liberated at the temperature of the still (160° ±) from a higher bromide (e. g., ferric bromide), resulting from impurity of iron in the arsenic. The least volatile fraction was grayish white after solidification.

In the second distillation, after removal of the light fraction, the tribromide was distilled upon copper strips, in order to eliminate free bromine if present. Reaction with the copper was evident for the color of the distillate disappeared and the copper became coated with a black substance, possibly $AsBr_3$, 7 Cu[6] or metallic arsenic or both. In the third distillation from the copper the light fraction, 2 (Fig 3), was nearly colorless when liquid and solidified to a white solid. The fourth and fifth fractionations also were from copper, but at that point its use was discontinued since no further effect was found. The heavy fraction 47 from the eleventh distillation was hydrolyzed with water and the product subjected to spectrographic examination in a graphite arc, with a Féry quartz spectrograph. No evidence of the presence of copper, tin or antimony could be detected. During the twelfth distillation the apparatus was opened to the air by the cracking of the Hempel column after three light fractions, 12, 13 and 14, had been removed.

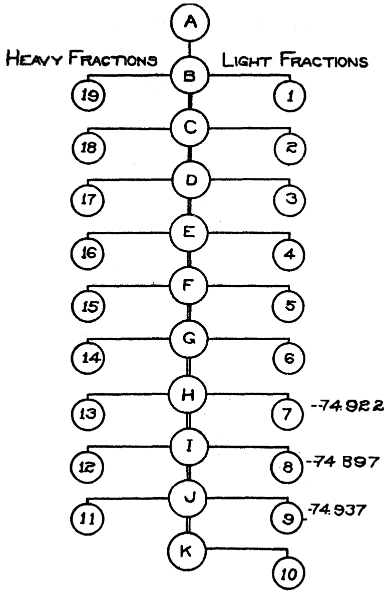

Fig. 2.—$AsBr_3$, I.

Since over 200 grams of material remained it was poured into a new apparatus, the air was flushed out by boiling the tribromide under reduced pressure and, after the system had been sealed, the fractionation was continued until only enough material remained to fill the six bulbs 28 to 33. An outline of the complete fractionation is shown in Fig. 3, with the atomic weights corresponding to the fractions analyzed.

The method of analysis was as follows. The exhausted sealed bulb containing the tribromide was weighed under water of known temperature by means of a tared platinum basket. Then it was cleaned, dried and weighed by substitution. At the same time the density of the air was found by weighing a standardized sealed glass globe.[7] Next the bulb was broken under 100–200 ml. of ammonia in a closed flask with a ground stopper, and after two to three hours the glass fragments were collected and weighed.

After a preliminary investigation the method of collecting the glass on a filter paper was given up because of the great difficulty in washing clean a filter through which the ammoniacal arsenite solution had been passed, even if the filter is subsequently washed with dilute nitric acid. On the other hand, platinum-sponge Gooch crucibles were found more satisfactory, for the excess in weight found when empty glass bulbs were

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(6) Hilpert and Herrmann, *Ber.*, **46**, 2224 (1913).

(7) Baxter, THIS JOURNAL, **43**, 1317 (1921).

broken under ammoniacal arsenite and the fragments, after being collected on a weighed crucible, washed with one per cent. nitric acid, was found to be 0.10 mg. as the average of six experiments varying from 0.16 to 0 04 mg. This observed excess in weight was applied as a correction in early analyses. In later analyses the glass was treated with hot 20% nitric acid, since it was found that glass so treated retained nothing from the arsenic solution, and no correction was applied. From the weight and volume of the bulb and the weight of the glass the weight of the tribromide in vacuum was found. Then a quantity of the purest silver[8] as nearly as possible equivalent to the tribromide was weighed out and dissolved slowly in nitric acid with especial pains to avoid loss by spattering. After dilution until 0.08 to 0.1 normal the silver solution was quantitatively added to the bromide solution, which had been made acid with nitric acid and possessed approximately the same concentration as the silver nitrate. Occasional agitation for a period of a week followed and then portions of the solution were tested in a nephelometer for excess of bromide or silver. If a deficiency of either was found 0.01 normal solution was added and the nephelometric test repeated until the exact end-point had been reached. The process of testing the solutions in most cases extended over six to seven months so that occluded material so far as possible should have opportunity for extraction. In fact changes amounting to +0.1 mg. of silver on an average occurred between the second and the sixth month. This is in accord with the evidence secured in an investigation by Baxter and Greene[9] in this Laboratory in which it was found that in the

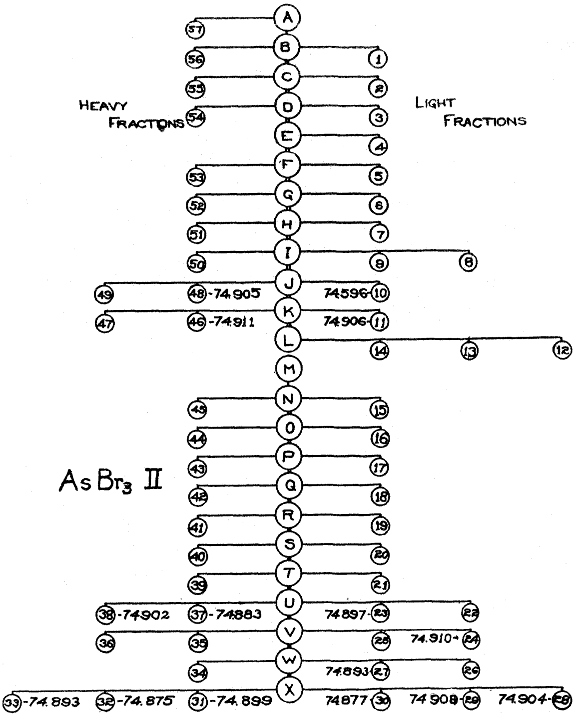

Fig. 3.—$AsBr_3$, II.

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(8) For an outline of the method of purification see Baxter and Ishimaru, THIS JOURNAL, 51, 1730 (1929).

(9) Baxter and Greene, *ibid*, 53, 611 (1981)

precipitation of ammonium bromide by silver nitrate a dilution of 0.03 normal was necessary to prevent occlusion of bromide although with ammonium chloride a concentration of 0.1 normal was apparently safe. How much effect this may have had in earlier work with bromides is difficult to determine.

Both the bulb and the silver were weighed by substituting weights for the carefully tared object. Weights were standardized by the Richards substitution method.[10] Vacuum corrections and the densities on which they were based are as follows:

	Density	Vacuum correction per gram
Air, 0° and 760 mm.	0.001293	
Weights	8.3	
Glass	2.50	+O. 000335
Silver	10.49	−0.000031

TABLE I

ATOMIC WEIGHT OF ARSENIC

Ag = 107.880 $AsBr_3$:3Ag Br = 79.916

Analysis	Fraction of $AsBr_3$	$AsBr_3$ in vacuum, g.	Ag in vacuum, g.	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vac., g.	Ratio $AsBr_3$:3Ag	At. wt. of arsenic
			Series 1				
1	8	10.00486	10.28800	+0.00287	1.0.29087	0.972207	74.897
2	9	9.64625	9.91934	+ .00142	9.92076	.972330	74.937
3	7	13.92585	14.32125	+ ,00155	14.32280	,972285	74.922
					Average	.972272	74.919
			Series 2				
1	10	5.73208	5.89407	−0.01120	5.88287	(0.974368)	(75.596)
2	48	6.63538	6.82552	− ,00062	6.82490	.972231	74.905
3	11	8.10704	8.33965	− .00111	8.33856	,972235	74.906
4	46	8.02860	8.25943	− .00168	8.25775	,972250	74.911
5	23	5.04824	5.19142	+ .00112	5.19255	.972208	74.897
6	37	7.27190	7.47838	+ ,00171	7.48011	,972165	74.883
7	38	7.70301	7.92164	+ .00145	7.92309	,972223	74.902
8	24	7.55491	7.76979	+ .00077	7.77056	.972248	74.910
9	29	6.49903	6.68397	+ ,00062	6.68459	,972241	74.908
10	30	6.14542	6.31998	+ ,00152	6.32150	,972146	74.877
11	31	6.74221	6.93428	+ ,00062	6.93490	,972214	74.899
12	32	6.80346	6.99675	+ .00170	6.99845	.972138	74.875
13	33	5.84643	6.01332	+ .00030	6.01362	,972195	74.893
14	27	8.16037	8.39234	+ .00142	8.39376	.972195	74.893
15	28	7.54923	7.76450	+ .00038	7.76488	,972228	74.904
			Average, omitting Analysis 1			.972208	74.897
			Average. omitting Analyses 1, 10, 12			,972219	74.901

Although the three specimens of tribromide used in Series 1 were consecutive light fractions, falling as they do in the latter part of the fractionation they may be considered to represent fairly the purest portion of the first preparation. This material was never as satisfactory as the second and in view of the small number of analyses and the somewhat less satisfactory concordance of results, the average of the series is chiefly valuable as a confirmation of the result of the second series.

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(10) Richards, THIS JOURNAL, 22, 144 (1900).

The analyses of the fractions of the second sample of tribromide, with the exception of the first, which seems to have been affected by some gross error, show no systematic variation. In some of the earlier analyses of this series it became evident that the interior wall of the flask in which the bulbs of tribromide were broken had been slightly scratched by the glass fragments, but since the analyses in which the scratched flask was used (2–9) were on the whole slightly higher than those carried out with a new flask (10–15), no appreciable error can be ascribed to this source. In Analyses 2–4 the samples used were collected immediately after the distillation from copper, but the results do not differ by a significant amount from those obtained with later fractions.

If the results are arranged in the order of decreasing volatility of material there is no apparent trend.

Fraction	Atomic weight	Fraction	Atomic weight
10	(75.596)	31	74.899
11	74.906	32	74.875
23	74.897	33	74.893
24	74.910	37	74.883
27	74.893	38	74.902
28	74.904	46	74.911
29	74.908	48	74.905
30	74.877		

The average value of all the results excluding that of Fraction 10, 74.897, differs by only 0.004 unit from the average obtained by excluding those of Fractions 30 and 32, 74.901. The apparent atomic weight of arsenic by this method therefore seems to be not far from 74.90.

The Analysis of Arsenic Trichloride

Antedating the investigation upon arsenic tribromide described above, a preliminary series of experiments with arsenic trichloride had been completed. In fact it was the unexpected outcome of these earlier experiments which led to the later work. In this earlier work[11] arsenic trichloride was fractionally distilled in vacuum and various fractions were analyzed by comparison with silver.

The original material was synthesized by heating metallic arsenic in a hard glass tube in a current of chlorine drawn from a cylinder of liquid material. Although presumably dry at the outset, the chlorine was passed over concentrated sulfuric acid and phosphorus pentoxide. After standing for some time over metallic arsenic the product was twenty-five times distilled in exhausted glass apparatus without the use of fractionating columns. In every distillation both more and less volatile fractions were removed.

After the sixteenth distillation the apparatus was accidentally opened to the air. The material was thereupon poured into a new distilling bulb connected with a special valve and, after this had been exhausted and flushed by boiling, the distillation was continued.

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(11) Begun by M. J. Dorcas and completed by E. W. Scripture.

In addition four (26–29) distillations with fractionating columns were carried out at the end, all of the residual material being finally collected in eight small bulbs.

The residue from the second distillation, Fraction 84, after hydrolysis was found by spectroscopic analysis to contain a trace of antimony but none could be detected in the residue from the third distillation (Fraction 82). The more volatile fraction from the first distillation (Fraction 1) was found to be apparently free from phosphorus. Residual impurities to be feared were therefore hydrogen chloride and oxychlorides or higher chlorides of arsenic. Since the first is more and the last two are less volatile than the trichloride, more or less rapid removal by fractionation is to be expected. An outline of the fractionation is given in Fig. 4.

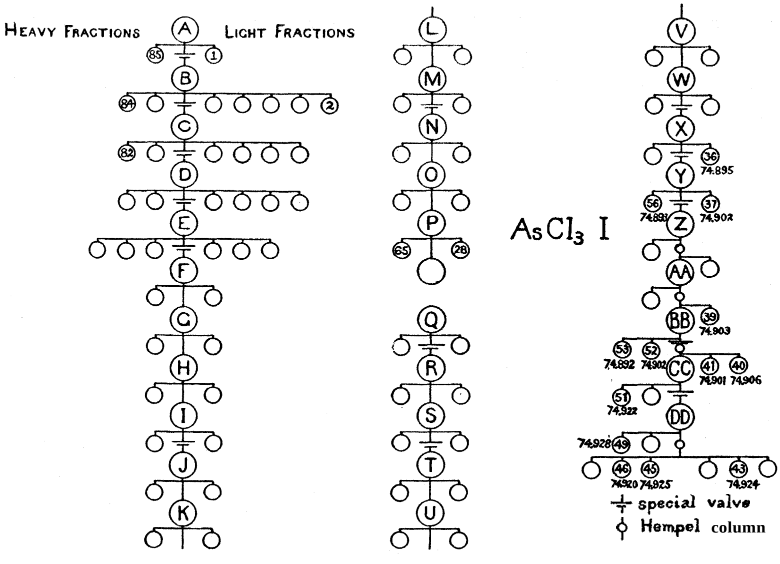

Fig. 4.

The analysis of the trichloride fractions was carried out as in the description of the analysis of the tribromide (page 1056) except that in the first eight analyses the glass of the bulbs was collected on filter paper which was then carefully charred and burned in a weighed platinum crucible, while in the last six it was collected on a platinum-sponge crucible. Later, in the work with arsenic tribromide which has already been described, it was found that it is difficult if not impossible to wash a filter entirely free from the arsenite solution so that the weights of arsenic trichloride in the first eight analyses are slightly too small and the resulting atomic weight of arsenic slightly too low. Even when the glass is collected on a platinum sponge crucible and ultimately washed with 1% nitric acid, as in the last six analyses, a slight excess in weight of the glass of 0.04 mg. was found as an average in blank experiments with empty glass bulbs A negative correction of this magnitude has therefore been applied to the weight of the glass in each analytical experiment. The following table contains the results of these analyses.

The second specimen of arsenic trichloride was prepared and fractionally distilled in vacuum by much the same method as that described for the tribromide[12] Crystalline commercial arsenic was first freed from moisture and arsenic trioxide by heating it to 350° in an exhausted hard glass tube Then the greater part of the arsenic was placed

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(12) *Carried out by W. E. Shaefer.*

TABLE II

Ag = 107.880 $AsCl_3$:3Ag Cl = 35.457

Analysis	Fraction	$AsCl_3$ in vacuum, g.	Ag in vacuum, g.	Ag added in solution, g.	Corr. wt. of Ag in vacuum, g.	Ratio $AsCl_3$: 3 Ag	At. wt. of arsenic
				Series 3			
1	36	5.58768	9.97046	0.00605	9.97651	0.560084	74.895
2	37	7.75110	13.83350	.00510	13.83860	.560107	74.902
3	56	9.14735	16.32589	.00640	16.33229	.560078	74.893
4	39	6.79634	12.13385	.00010	12.13395	.560109	74.903
5	40	6.07547	10.84693	−.00020	10.84673	.560120	74.906
6	41	5.07411	9.06125	−.00200	9.05925	.560103	74.901
7	53	6.33798	11.34328	−.02698	11.31630	.560075	74.892
8	52	6.90994	12.33893	−.00210	12.33683	.560107	74.902
					Average	.560098	74.899
				Series 4			
9	51	3.93552	7.02526	0.00035	7.02561	0.560168	74.922
10	49	5.41621	9.66859	.00000	9.66859	.560186	74.928
11	45	4.81464	8.59458	.00025	8.59483	.560179	74.925
12	43	4.66762	8.33241	.00000	8.33241	.560176	74.924
13	46	3.13878	5.60332	.00000	5.60332	.560164	74.920
					Average	.560175	74.924

in a hard glass tube connected at one end with a supply of pure dry chlorine. The other end of the hard glass tube delivered into a glass bulb containing the remainder of the arsenic. The chlorine was prepared from manganese dioxide and concentrated hydrochloric acid and after being thoroughly scrubbed with water was dried with concentrated sulfuric acid and phosphorus pentoxide. All the apparatus was constructed of glass with fused or ground joints. During the passage of the chlorine the arsenic was heated hot enough to ensure complete reaction of the chlorine. About 900 g. of trichloride was prepared.

After the trichloride had been allowed to stand in contact with the arsenic in the bulb for several days until it was colorless, it was poured into a distilling bulb attached to a special valve. The bulb was next placed in a bath of hot water and exhausted with an efficient water pump. This caused the trichloride to boil vigorously and displace the greater part of the air and the hydrogen chloride formed by hydrolysis during contact with the air in the transference. The bulb was then permanently sealed by fusing a capillary in the lead to the pump.

Since it was possible that the unexpectedly low atomic weight of arsenic which had so far been obtained by analysis of the trihalides might be due to residual chlorine or higher chloride, especial effort was now made to make certain that these impurities, if present, were eliminated. This was done by repeated distillation over arsenic at increasingly higher temperatures. First the trichloride was many times distilled from one bulb to another, both of which contained crystals of arsenic which had been heated in a vacuum, through Hempel columns also filled with arsenic crystals instead of glass beads.

Fractional distillation was then undertaken in apparatus similar to that shown in Fig. 1. During a distillation the still was heated in a water-bath to 50–60° and the receiving bulb was cooled with ice water. Under these conditions very efficient refluxing without choking occurred in the Hempel columns. The sample bulbs were usually cooled with carbon dioxide snow and alcohol, but sometimes merely with ice and salt. After thirteen fractional distillations had been carried out, the remaining material (80 cc.) was set aside for subsequent examination. The course of this fractionation is shown on the left-hand side of Fig. 5.

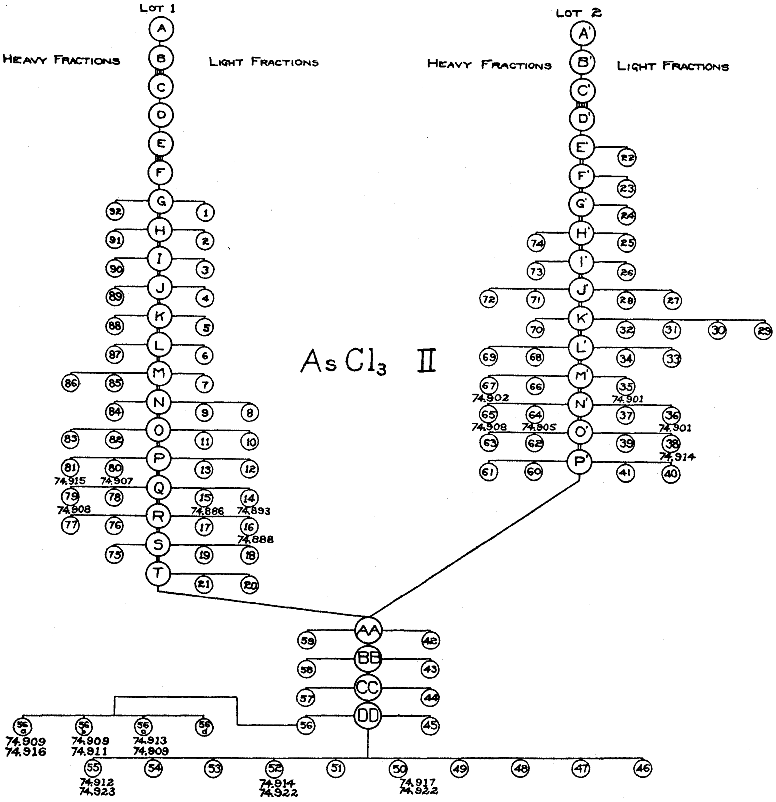

Fig. 5

Since the analysis of the fractions obtained in this preparation (Table III, Series *5)* still indicated a low value for the atomic weight of arsenic, the experiment was tried of passing the vapor of the trichloride through a tube filled with arsenic heated to a relatively high temperature. **A** new lot of trichloride was prepared exactly as before and after being boiled under low pressure to remove dissolved gases was distilled into an exhausted system consisting of two bulbs connected through a hard glass tube which terminated in ground glass joints and filled with arsenic which had been previously heated in vacuum. The ground joints fitted well but were not lubricated. Instead the joints were made vacuum tight by an outside layer of de Khotinsky cement. The trichloride was then five times distilled back and forth from one bulb to the other while the arsenic was heated to the temperature of sublimation. After transfer by distillation to a new exhausted system, fractionation of the product was carried on until twelve distillations had been made. The course of this fractionation is shown on the right-hand side of Fig. 5. The material remaining after the twelfth distillation (100 cc.) was then combined with the remainder from the previous preparation and the fractionation of the mixture continued as indicated in the lower part of **Fig.** 5. This treatment also failed to alter the composition of the trichloride (Table **III,** Series *6).*

Three groups of analyses of these arsenic trichloride fractions were made, covering the first and second preparations as well as the mixture of the two. In the first group not only were light and heavy fractions compared, but also the effect of oxidizing the arsenite before precipitation of silver chloride was investigated, although there is no reason to expect reduction of silver salts. The oxidation was accomplished in two experiments by adding hydrogen peroxide in essentially the theoretical quantities to oxidize the arsenite; in two experiments potassium bichromate was used for the purpose The oxidizing solution was added to the acidified solution of the arsenite through a funnel tube extending to the bottom of the solution. Although the bichromate was chloride free, the hydrogen peroxide contained a trace of chloride which was estimated quantitatively by means of a nephelometer and a corresponding correction applied.

The glass fragments were collected on a platinum sponge crucible as described on page 1056, and after the initial weighing were again twice washed with 5 normal nitric acid. The first washing usually produced a slight loss in weight, amounting on an average in eighteen experiments to 0.10 mg. The second washing was almost without effect, for the average of the very small change was 0.01 mg.

The precipitation of the silver chloride was carried out much as described on page 1057, but even greater pains were taken to prevent occlusion by the silver chloride by slow addition of the silver nitrate solution. That the silver chloride was really pure was shown by examining the arc spectrum of carefully washed material from two analyses in a Féry quartz spectrograph. No trace of arsenic could be detected.

In the last six analyses, as soon as the exact end-point had been found the silver chloride was determined gravimetrically. To do this, first an excess of about one gram of silver nitrate was added to the flask containing the analysis and after the solution had

TABLE III

ATOMIC WEIGHT OF ARSENIC

Ag = 107.880 $AsCl_3$:3Ag Cl = 35.457

Analysis	Fraction of $AsCl_3$	Oxidizing agent	$AsCl_3$ in vacuum, g.	Ag in vacuum, g.	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vacuum, g.	Ratio $AsCl_3$: 3Ag	At. wt. of arsenic
				Series 5				
1	80	None used	4.19732	7.49207	+0.00150	7.49357	0.560123	74.907
2	81	H_2O_2	4.98056	8.89089	+ ,00065	8.89154	,560146	74.915
3	14	None used	4.73909	8.45956	+ .00190	8.46146	.560079	74.893
4	15	H_2O_2	4.15568	7.41843	+ ,00166	7.42009	.560058	74.886
5	79	$K_2Cr_2O_7$	5.15747	9.20840	− ,00070	9.20770	.560126	74.908
6	16	$K_2Cr_2O_7$	5.29708	9.45821	− .00020	9.45801	.560063	74.888
						Average	.560099	74.900
				Series 6				
7	35		4.94345	8.82603	−0.00010	8.82593	0.560105	74.901
8	36		4.82524	8.61471	+ .00020	8.61491	,560103	74.901
9	64		3.84375	6.86270	− .00030	6.86240	.560117	74.905
10	65		4.28593	7.65215	− .00040	7.66175	.560124	74.908
11	38		4.62010	8.24886	− ,00080	8.24806	.560144	74.914
12	67		4.01638	7.17093	− .00020	7.17073	.560108	74.902
						Average	.560117	74.905
				Series 7				
13	50		5.10281	9.11017	−0.00050	9.10967	0.560153	74.917
14	52		5.06855	9.04884	− .00020	9.04864	,560145	74.914
15	55		5.29138	9.44726	− .00070	9.44656	.560138	74.912
16	56a		5.67514	10.13242	− .00060	10.13182	.560130	74.909
17	56b		5.14259	9.18160	− .00050	9.18110	.560128	74.909
18	56c		5.82250	10.39523	− .00050	10.39473	.560140	74.913
						Average	,560139	74.912
						Average of Series 5, 6 and 7	.560118	74.906
						Average of Series 6 and 7	,560128	74.909

TABLE IV

ATOMIC WEIGHT OF ARSENIC

Ag = 107.880 $AsCl_3$:3AgCl Cl = 35.457

Analysis	Fraction of $AsCl_3$	$AsCl_3$ in vacuum, g.	AgCl in vacuum, g.	Loss in wt. on fusion, g.	Dissolved AgCl, g.	Corr. wt. of AgCl in vac., g.	Ratio $AsCl_3$: 3 AgCl	At. wt. of arsenic
				Series 8				
19	50	5.10281	12.10317	0.00047	0.00069	12.10339	0 421602	74.922
20	52	5.06865	12.02154	,00031	.00090	1202213	.421602	74.922
21	55	5.29138	12.56012	.00034	,00083	12.55061	,421603	74.923
22	56a	5.67514	13.46109	.00042	.00073	13.46140	.421586	74.916
23	56b	514259	12.19805	,00031	,00074	12.19848	.421576	74.911
24	56c	582250	13.81091	.00024	.00077	1381144	,421571	74909
						Average	,421590	74.917

been vigorously shaken, it was cooled in an ice-bath. The precipitate was then washed thoroughly by decantation with an ice-cold 0.0003 normal solution of silver nitrate, and was transferred to a weighed platinum-sponge Gooch crucible by means of ice cold water. After being dried at 300° for twenty hours the precipitate was weighed. The bulk of the precipitate was next transferred to a porcelain crucible and the moisture lost by fusion determined.

The precipitating flask was rinsed with dilute ammonia and the rinsings were added to the water used in the transfer of the silver chloride. By nephelometric comparison with standard chloride solutions the chloride content of this solution was found, and applied as a positive correction to the weight of silver chloride. The solubility of silver chloride in the chilled silver nitrate washings was assumed to be 0.02 mg. per liter. Since no opalescence whatever could be produced in the original supernatant solution by further addition of silver nitrate the solubility of the silver chloride in this solution was neglected. In Table III a vacuum correction of +0.000071 per gram has been applied to the observed weights of silver chloride. This is based on the density 5.56.

In Table V the results of Series 5 are grouped according to volatility of the fractions

TABLE V

Light fraction	Oxidizing agent	Atomic wt. arsenic
14	None	74.893
15	H_2O_2	74.886
16	$K_2Cr_2O_7$	74.888
	Average	74.889
Heavy fraction		
79	$K_2Cr_2O_7$	74.908
80	None	74.907
81	H_2O_2	74.915
	Average	74.910

Apparently the use of an oxidizing agent is without influence. The light fractions however yield a somewhat lower value than the heavy fractions, and this difference might lead to the conclusion that the purification of the trichloride was not complete at the stage when these fractions were removed. A similar comparison of the results of Series 6 which represent fractions removed at a similar stage in the purification of the second lot of trichloride, shows no indication of any difference between light and heavy fractions, nor between these and fractions obtained in a still later stage in the fractionation (Table III, Series 7).

TABLE VI

Light fraction	Atomic weight	Heavy fraction	Atomic weight
35	74.901	64	74.905
36	74.901	65	74 908
38	74.914	67	74.902
Average	74.905	Average	74.905

On the other hand, the gravimetric determination of the silver chloride leads to a slightly higher value for the atomic weight of arsenic, which indicates that less silver chloride was obtained than corresponds to the quantity of silver used in the comparison. The last two are compared in the following table.

TABLE VII

Analyses	Fraction	Ratio Ag:AgCl
13 and 19	50	0.752654
14 and 20	52	,752665
15 and 21	55	.752677
16 and 22	56a	.752657
17 and 23	56b	.752643
18 and 24	56c	.752617
	Average	.752652

Theoretical (Ag = 107.880; Cl = 35.457) 0.752627

The deficiency of silver chloride amounts to 0.003% or 0.4 mg. in the quantities obtained in the above experiments.

The following table summarizes our work on arsenic trihalides by comparison with silver and silver chloride.

TABLE VIII

Series 1	$AsBr_3:3Ag$	74.919
Series 2	$AsBr_3:3Ag$	74.897
Series 3	$AsCl_3:3Ag$	74.899
Series 4	$AsCl_3:3Ag$	74.924
Series 5	$AsCl_3:3Ag$	74.900
Series 6	$AsCl_3:3Ag$	74.905
Series 7	$AsCl_3:3Ag$	74.912
Series 8	$AsCl_3:3AgCl$	74.917
	Average	74.909

Average weighted according to number of analyses 74.906

Although the third decimal place in the averages must beyond question be very uncertain, the evidence presented above points to a value not far from 74.91, 0.02 unit lower than the present International value.

While the reason for the discrepancy between Krepelka's and our results is not apparent, representing as they do work of a very similar character, certainly there is little question that the old value for arsenic, 74.96, adopted in the national and international tables until 1931 is too high. The bearing of Aston's results on this problem is not particularly decisive. The present accuracy claimed for the mass spectrograph is 1/10,000 and the uncertainty of the conversion factor is fully as large. Therefore it is doubtful whether the atomic weight of arsenic could at present be determined with the mass spectrograph within 0.01 unit aside from the possibility that arsenic may contain small amounts of undiscovered isotopes.

Summary

1. The preparation of pure arsenic trichloride and tribromide is described.

2. By analysis of the trihalides the atomic weight of arsenic is found to be 74.91.

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Reactions of Ethylene Oxide. I. The Action of Ethylene Oxide on Diethylamine

BY A. J. W. HEADLEE, A. R. COLLETT AND C. L. LAZZELL

Introduction

Previous to the recent paper of Horne and Shriner[1] the literature contained no satisfactory directions for the preparation of diethylaminoethanols from ethylene oxide and diethylamine. Simultaneously with Horne and Shriner, the present authors, using a different method of preparation, obtained products whose physical properties do not agree with those obtained by the above workers. The authors do not agree with Horne and Shriner's statement that ethylene oxide does not react with their solvent, methyl alcohol, an appreciable reaction being easily obtained at 55°. By successive additions of ethylene oxide to diethylamine and the resulting products the following compounds were prepared and will be referred to hereafter by the Roman numeral assigned to each.

I $(C_2H_5)_2NCH_2CH_2OH$
II $(C_2H_5)_2NCH_2CH_2OCH_2CH_2OH$
III $(C_2H_5)_2N(CH_2CH_2O)_2CH_2CH_2OH$
IV $(C_2H_5)_2N(CH_2CH_2O)_3CH_2CH_2OH$
V $(C_2H_5)_2N(CH_2CH_2O)_4CH_2CH_2OH$
VI $(C_2H_5)_2N(CH_2CH_2O)_5CH_2CH_2OH$
VII $(C_2H_5)_2N(CH_2CH_2O)_6CH_2CH_2OH$

Experimental

Preparation of Diethylaminoethanol.—38.3 grams of diethylamine (b. p. 55–57°) and 23.5 g. of ethylene oxide were caused to react in a copper autoclave of 500-ml. capacity at 100°. The reaction was complete within one hour; 49.6 g. of (I) was obtained, a yield of 81%. The reaction could be completed in two to ten minutes in the presence of small quantities of water, but this greatly increased the difficulties of separating the products. The reaction was also carried out in the presence of ether and alcohol as solvents but with a decrease in the rate of the reaction. Diethylaminoethanol

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(1) Horne and Shriner, THIS JOURNAL, 54, 2925 (1932).

and ethylene oxide were autoclaved yielding (II) (II) was then autoclaved with ethylene oxide to produce (III). This process was continued until sufficient quantities of each compound were obtained for purification. On careful fractional vacuum distillation, colorless products were obtained for compounds I–VII.

Preparation of the *p*-Nitrobenzoate of (II).—4.2 grams of (II) in benzene was added to 4 6 g. of *p*-nitrobenzoyl chloride. The crystals (m. p. 128.5") obtained were soluble in water, alcohol, chloroform, and only slightly soluble in acetone.

Anal. Calcd for $(C_2H_5)_2NHCl(C_2H_4O)_2COC_6H_4NO_2$: Cl, 10.2; mol. wt. 347. Found: Cl, 10.06; mol. wt., 344.

In Table I are collected the pertinent data relating to the compounds prepared. The data of Horne and Shriner are also presented here in order to form a basis of comparison.

TABLE I

PROPERTIES OF THE ETHANOL AMINES

	I	II	III	IV	V	VI	VII
B. p., °C.	160[a]	135	163–165	185–188	182–184	254–259	205–209
Mm.	741	46	30	53	9	36	4
B. p., °C., H & S.[b]	163	92–95	123–128	164–172	190–200		
Mm.	760	7	7	7	7		
n_D^{25}	1.4389	1.4464	1.4501	1.4529	1.4566	1.4592	1.4620
H. & S.[b]	1.4400	1.4457	1.4534	1.4570	1.4622		
M_D^{25} Calcd.	34.94	45.82	56.70	67.58	78.46	89.63	100.51
Found	34.94	45.61	56.61	67.85	78.70	89.25	99 95
Found, H. & S.[b]	35.81	45.65	56.80	66.31	74.92		
$d_{Abs.}^{25}$	0.8800	0.9421	0.9753	0.9905	1.0128	1.0325	1.0474
H. & S.[b]	0.8575	0.9371	0.9734	1.0206	1.048		
$\eta_{Abs.}^{25}$	0.0405	0.0856	0.1284	0.1596			
γ 26.5"	27.50	30.05	31.26	32.05	33.47	34.65	35.51
Mol. wt. Calcd.	117	161	205	249	293	337	381
Found	116	171	223	245	281	321	367
N_2, %, Calcd.	11.95	8.69	6.83	5.62	4.77	4.15	3.67
Found	11.88	8.40	6.51	5.74	4.82	3.96	3.80

[a] The following boiling points were obtained for (I): 55° (10 mm.); 100" (80 mm.); 96° (73 mm.). [b] (H. & S.) Data of Horne and Shriner.[1] For comparison their specific gravities were converted to absolute densities.

All thermometers were checked against certified thermometers and were corrected for emergent stem. The refractive indices were determined with an Abbé refractometer; the density with an 8-cc. pycnometer; the viscosity with an Ostwald viscometer; the surface tension by the Du Noüy method (corrected by the formula of Harkins and Jordan);[2] the molecular weights by the freezing point method using benzene as a solvent; the nitrogen content by the Kjeldahl method, and by titration with sulfuric acid.

Discussion of Results

In Fig. 1 are plotted curves showing the change in density and refractive index with increase in molecular weight. The continuous addition of ethylene oxide to the aminoethanols suggests the possibility of preparing

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(2) Harkins and Jordan. THIS JOURNAL, 62, 1751 (1930).

a series of ethoxyethanols of indeterminate length. No indication of a decrease in activity of the hydroxyl group with increasing length of the chain was noted. Thus the number of additions seems to be limited only by the stability of the chain. This offers a possible explanation of the so-called polymers[3] of ethylene oxide described in the recent literature. The continuous addition of ethylene oxide to a very limited number of hydroxyl groups might produce a compound whose empirical formula would be very near that of ethylene oxide. In fact when the authors autoclaved 1.5 g. of diethylaminoethanol with 28 g. of ethylene oxide, no uncombined ethylene oxide was detected. The resulting product was a very highly viscous liquid. The proportions of the reactants used would indicate that as an average the molecules of this product contain approximately fifty —CH_2CH_2O— groups, provided the ethylene oxide continued to add on to each newly formed hydroxyl group. This phase of the work is now being investigated.

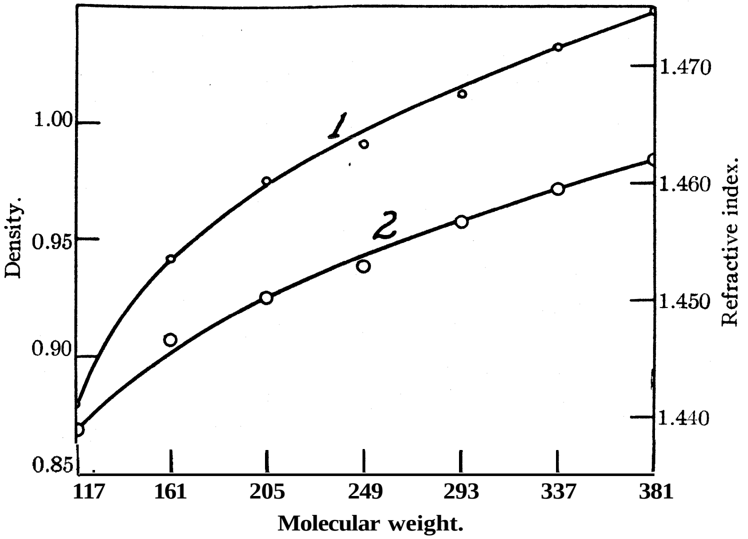

Fig. 1.—Physical properties of the amines: curve 1, density; curve 2, refractive index.

The authors wish to acknowledge their indebtedness to the Carbide and Carbon Chemicals Corporation, Charleston, West Virginia, for the supply of ethylene oxide used in this investigation.

Summary

1. Methods for the preparation of diethylaminoethanol giving yields of 80–87% are described. Some physical properties of this compound have been determined.

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(3) Staudinger and Schweitzer, *Ber.*, **62**, 2395 (1929)

2. A series of diethylaminoethoxyethanols have been prepared and some of their physical properties determined. Two members of this series have not been reported previously.

MORGANTOWN, WEST VIRGINIA

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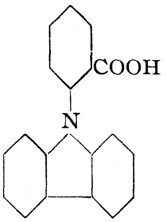
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of N-Phenylpyrroles. XXIX.[1] Preparation and Properties of o-N-Carbazyl- and o-N-(3-Nitrocarbazylj-benzoic acid

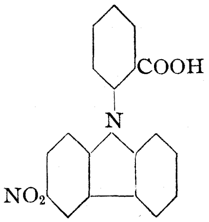
BY W. I. PATTERSON[2] AND ROGER ADAMS

A discussion of the optical isomerism of substituted phenylpyrroles and dipyrryls[3] has been given in previous papers and representative compounds of both classes have been prepared and resolved (III and IV). The experimental evidence all pointed to the conclusion that the isomerism is essentially of the same type and due to essentially the same causes as are found in substituted diphenyls.

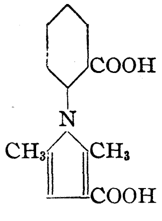
The present investigation has involved the extension of this work to certain substituted N-phenylcarbazoles. In o-N-carbazylbenzoic acid (I) there is a symmetrical substitution of the pyrrole ring and, therefore, the compound should be resolvable only if the nitrogen atom retains a more or less fixed tetrahedral structure. No resolution was accomplished. On the other hand, if a substituting group is introduced into the carbazole nucleus, unsymmetrical substitution of the pyrrole is present and substitution conditions resembling those necessary for resolution in the diphenyl series obtain. The *o*-(3-nitrocarbazyl)-benzoic acid (II) was resolved into enantiomorphic forms. The fact that the introduction of a substituting group so far removed from the carbazole nitrogen atom is all that is necessary to render the molecule capable of being resolved, is a potent argument against the probability that optical activity is due to the nitrogen atom.



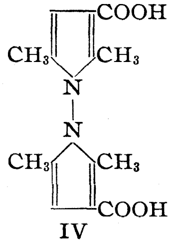
I



II



III



IV

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[1] For the last paper, XXVIII, see Kleiderer and Adams, THIS JOURNAL, 55, 716 (1933).

[2] The experimental work was done by W. I. Patterson and is part of his thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[3] Bock and Adams, THIS JOURNAL 53, 374, 3519 (1931); Chang and Adams, *ibid.*, 53, 2353 (1931)

The active forms of *o*-(3-nitrocarbazyl)-benzoic acid are racemized very slowly at room temperature in chloroform, but readily by warming in chloroform, alcohol, or sodium hydroxide solution (see Table I). Racemization takes place much more easily than in the active forms of N-2-carboxyphenyl)-2,5-dimethyl-3-carboxypyrrole (III), indicating that the methyls have a greater interfering effect than the CH of the benzene nucleus in compounds of this type.

Experimental

The carbazylbenzoic acids were prepared by condensation of *o*-iodobenzoic acid with carbazole or 3-nitrocarbazole in boiling nitrobenzene with solid potassium hydroxide.

o-Carbazylbenzoic Acid and its Salts.—This compound was prepared in 66% yields by the method of Eckert, Seidel and Endler;[4] m. p. when pure 184". The brucine salt was formed in ethyl acetate. On long standing, large colorless rhombohedra separated, m. p. 214–215°. No resolution was observed after many trials. In one experiment an ethyl acetate solution of the brucine salt was evaporated slowly at room temperature and six separate fractions of salt taken. The rotation of the mother liquor was determined after each removal and an allowance was made for each change in concentration. The rotation of the solution remained practically constant. An alcoholic solution at 0° with concentrated hydrochloric acid gave, on addition of water, colorless white needles of the inactive acid.

The strychnine, morphine, quinine and dicinchonine salts were also prepared, but in no instance could two different salts be obtained. The method of preparation of the salts and the constants for them are given in Table II.

o-(3-Nitrocarbazyl)-benzoic Acid and its Resolution.—The compound was prepared by the condensation of o-iodobenzoic acid with 3-nitrocarbazole[5] by the method of Hayashi.[6] The yields were poor, 10–35%. The product was purified by repeated recrystallization from hot glacial acetic acid followed by one crystallization from alcohol after treatment with norite. Lemon yellow needles were obtained, m. p. 226–227" (corr.) (Hayashi 230°).

A hot solution of 2.2 g. of *o*-(3-nitrocarbazyl)-benzoic acid in 20 cc. of anhydrous ethyl acetate was added to a hot solution of 2.6 g. of anhydrous brucine in 60 cc. of anhydrous ethyl acetate. After standing for twenty-four hours at room temperature, a crystalline precipitate weighing 2.5 g. resulted. This fraction was purified by dissolving in chloroform and adding an excess of absolute alcohol. After twenty-four hours at room temperature the product had separated as large lemon colored crystals, m. p. 246–247°.

Rotation. 1.2574 g made up to 25 cc with chloroform at 20° gave α_D $-1.05°$; $l = 2$; $[\alpha]^{20}_{D}$ $-10.44°$

Anal. Calcd. for $C_{42}H_{38}O_8N_4$: N, 7.71; C, 69.39; H, 5.27. Found: N, 7.78; C, 69.29; H, 5.33.

The filtrate from the 2.5 g. fraction was allowed to evaporate to half its volume and a small amount of crystalline material which separated was filtered and consisted primarily of the less soluble salt. The more soluble salt remained as a resin after all the solvent had been evaporated from the filtrate. All attempts to crystallize the salt failed. The ro-

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(4) Eckert, Seidel and Endler, *J. prakt. Chem.*, **104**, 85 (1922).

(5) Ruff and Stein, *Ber.*, **34**, 1677 (1901).

(6) Hayashi, *Bull. Inst. Phys.-Chem. Res. (Tokyo)*, **9**, 970 (1930).

TABLE I

Acid	Solvent	Concn.[c]	α_D^{20}	$[\alpha]_D^{20}$	Temp., rac., °C.	k	Av. deviation	Half-life, min.
d	Chloroform	1.78	+0.15	+ 7.0	60	0.01	0.0006	72
l	Abs. alcohol	1.80	−1.51	−45.0	78.5	.254	.034	29
l	0.1 *N* NaOH	0.88	−0.91	−51.7	27[a]	.00032	.0001	2190
d	Na in alcohol[b]	0.80	+1.08	+67.3	27[a]	.00065	.00002	1080

[a] Completely racemized in 140 and 97 hrs., respectively. [b] 0.5 g. of sodium in 50 cc. of absolute alcohol. [c] Grams per 100 cc.

TABLE II

ALKALOIDAL SALTS[a] OF *o*-CARBAZYLBENZOIC ACID

Alkaloid	Wt., g.	Solv. (dry)	Solv. cc.	Acid, wt.	Solv. (dry)	Vol., cc.	Formula	Concn.[b]	α_D^{25c}	$[\alpha]_D^{25}$	Calcd. N, %	Found N, %
Brucine	2.7	Eth. ac.	70	2.0	Eth. ac.	10	$C_{42}H_{39}O_6N_3$	0.63	+0.23	+ 18.2	6.16	6.35
Strychnine	2.5	$CHCl_3$	25	2.1	Eth. ac.	25	$C_{40}H_{35}O_4N_3$	1.61	−0.53	− 16.4	6.76	6.52
Morphine	2.1	CH_3OH	30	2.0	Eth. ac.	20	$C_{36}H_{34}O_6N_2$	0.81	−0.43	− 54.0[c]	4.75	4.94
Quinine	0.8	Eth. ac.	25	0.7	.....	..	$C_{39}H_{37}O_4N_3$	0.43	−0.46	− 26.5	6.87	6.84
Cinchonine	0.9	$CHCl_3$	200	1.7	.....	..	$C_{57}H_{48}O_5N_4$	0.35	+1.15	+166.2	6.45	6.39

[a] The salts crystallized from the solutions after standing at room temperature for a few hours, with the exception of the dicinchonine salt which required a week.

[b] Grams per 100 cc.

[c] Rotations were measured at 25° and in chloroform solution with sodium light in tubes 2 dm. long; for the morphine salt dioxane was the solvent used.

tation of the crude material varied from $[\alpha]^{20}_{D}$ +21.7 to +46.7°. It decomposed at 160–180°.

Rotation. 0.3104 g. made up to 25 cc. with chloroform at 20° gave α_D +0.90°; $l = 2$; $[\alpha]^{20}_{D}$ +21.7°.

d- and **l-o-(3-nitrocarbazyl)-benzoic** Acid.—The active acids were liberated from the individual salts by shaking with ether and 6 N hydrochloric acid in a separatory funnel until complete solution of the solid matter occurred. Regardless of the rate of evaporation of the ether solution, either moist or dry, an oil, sometimes containing a small amount of crystalline material, was always obtained when the evaporation was carried out at room temperature.? Alcohol and chloroform gave similar results. After long standing in a desiccator the oil gradually changed to a glassy solid which, on powdering, melted at 225–226°, and gave a negative test for brucine with concentrated nitric acid. The rotation of the acid thus obtained from different samples of the less soluble salt varied from $[\alpha]^{20}_{D}$ −56° to $[\alpha]^{20}_{D}$ −62°.

Rotation. 1-Acid, 0.2924 g. made up to 25 cc. with chloroform at 20° gave α_D −1.45"; $l = 2$; $[\alpha]^{20}_{D}$ −62".

Anal. Calcd. for $C_{19}H_{12}O_4N_2$: N, 8.44. Found: N, 8.36.

The d-acid obtained similarly from the crude more soluble salt was also an oil which gradually solidified. A rotation was taken on the crude acid melting at 224–225°. Different samples of the salt produced acids with widely variable rotations, but the rotation was always positive.

Rotation. d-Acid, 0.2497 g. made up to 16.1 cc. with chloroform at 20° gave *a,,* +1.26°; $l = 2$; $[\alpha]^{20}_{D}$ +40.57°.

Racemization Experiments.—Data on racrmization tests on the active acid are given in Table II.

Summary

1. o-N-Carbazylbenzoic acid and *o*-N-(3-nitrocarbazyl)-benzoic acid were prepared by condensing carbazole or 3-nitrocarbazole with *o*-iodobenzoic acid.

2. o-N-(3-Nitrocarbazy1)-benzoicacid was resolved into enantiomorphs but o-N-carbazylbenzoic acid could not be resolved.

3. With a fixed asymmetric structure for nitrogen both compounds should be resolvable. It appears that the fundamental conditions found necessary for resolution of diphenyl compounds hold in this series.

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(7) After the alcoholic solution of the oil had been boiled for a few minutes, dilution with water until a permanent clouding occurred, followed by cooling, gave a crystalline acid which melted at 226–227°. This crystalline acid always possessed optical activity, provided that the heating was not continued too long.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction between Unsaturated Ketones and Organic Magnesium Compounds. The Secondary Products

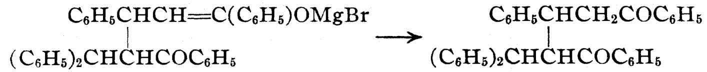
BY E. P. KOHLER AND W. D. PETERSON

It is common knowledge that in the reaction between α,β-unsaturated ketones and Grignard reagents it is necessary to use a large excess of reagent in order to prevent the formation of secondary products, but of the nature of these products little is known. In the first paper of this series[1] one of these secondary products was isolated and analyzed, namely, the compound that is formed by adding phenylmagnesium bromide to benzal acetophenone. The composition and molecular weight of this compound were established correctly, but the formula that was proposed for it has long since been untenable because it was based on an erroneous interpretation of the primary reaction.

With the recent discovery that the primary products of this reaction behave like the enolates of β-ketonic esters and β-diketones,[2] the secondary products acquired a new interest. It seemed not unlikely that these products are formed in a second reaction which differs from the first only in the character of the magnesium derivative. In the case of benzal acetophenone and phenylmagnesium bromide the successive steps would be represented as follows

$$C_6H_5CH{=}CHCOC_6H_5 + C_6H_5MgBr \longrightarrow \underset{\text{I}}{(C_6H_5)_2CHCH{=}C(C_6H_5)OMgBr}$$

$$C_6H_5CH{=}CHCOC_6H_5 + (C_6H_5)_2CHCH{=}C(C_6H_5)OMgBr \longrightarrow$$



$$\begin{array}{c} C_6H_5CHCH{=}C(C_6H_5)OMgBr \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array}$$

II III

We have found that this surmise is correct. By taking advantage of the reaction between alpha bromo ketones and Grignard reagents[2] it is possible to secure a solution of the magnesium derivative represented by I that is free from the Grignard reagent. When an equivalent quantity of benzal acetophenone was added to such a solution it was converted, almost quantitatively, into the diketone represented by III. The proof of the structure of this diketone is as follows.

The substance reacts with two moles of methylmagnesium iodide without liberating gas; it therefore is a diketone. It readily forms a mono-oxime but, as would be expected in view of the number of substituents around the carbonyl groups, it cannot be converted into a di-oxime by the usual methods. By means of a Reckmann rearrangement, followed by hydrolysis of the product, the oxime was degraded to the corresponding acid and aniline.

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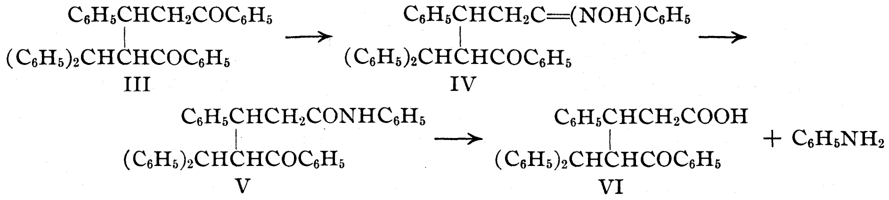
(1) Kohler, *Am. Chem. J.*, **29**, 352 (1903).

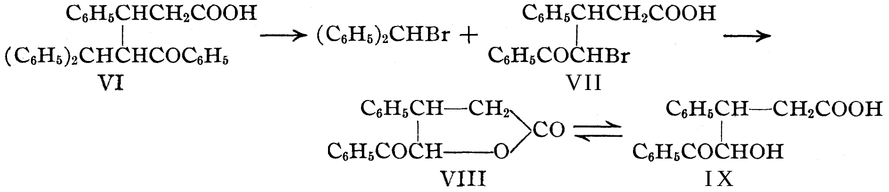
(2) Kohler and Tishler, THIS JOURNAL, **54**, 1594 (1932).



$$\begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{III} \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH_2C{=}(NOH)C_6H_5 \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{IV} \end{array} \longrightarrow$$

$$\begin{array}{c} C_6H_5CHCH_2CONHC_6H_5 \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{V} \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH_2COOH \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{VI} \end{array} + C_6H_5NH_2$$

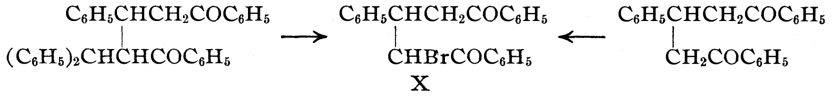
The result is a 6-ketonic acid. Our plan was to brominate this acid and prove that the product was a y-bromo acid by converting it into a lactone. The plan went awry because the bromination took an unexpected course. Fortunately, however, the result is equally conclusive.



$$\begin{array}{c} C_6H_5CHCH_2COOH \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{VI} \end{array} \longrightarrow (C_6H_5)_2CHBr + \begin{array}{c} C_6H_5CHCH_2COOH \\ | \\ C_6H_5COCHBr \\ \text{VII} \end{array} \longrightarrow$$

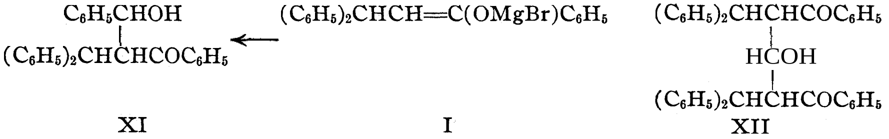
$$\begin{array}{c} C_6H_5CH{-}CH_2\diagdown \\ |\qquad\qquad\ CO \\ C_6H_5COCH{-}{-}O\diagup \\ \text{VIII} \end{array} \rightleftharpoons \begin{array}{c} C_6H_5CH{-}CH_2COOH \\ | \\ C_6H_5COCHOH \\ \text{IX} \end{array}$$

This unexpected course of the bromination, of which another example had become known very much earlier,[3] enabled us to relate the diketone directly to a substance of known structure.



$$\begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ CHBrCOC_6H_5 \\ \text{X} \end{array} \longleftarrow \begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ CH_2COC_6H_5 \end{array}$$

In the light of these results it is evident that the primary addition products can combine with unsaturated ketones in the same manner as Grignard reagents and sodium enolates. They can also combine with substances which have active carbonyl groups. Thus when benzaldehyde was added to a solution containing the same primary addition product, it precipitated the magnesium derivative of the corresponding ketol, and a similar product was obtained from ethyl formate.



$$\begin{array}{c} C_6H_5CHOH \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \\ \\ \text{XI} \end{array} \longleftarrow \begin{array}{c} (C_6H_5)_2CHCH{=}C(OMgBr)C_6H_5 \\ \\ \\ \\ \\ \text{I} \end{array} \qquad \begin{array}{c} (C_6H_5)_2CHCHCOC_6H_5 \\ | \\ HCOH \\ | \\ (C_6H_5)_2CHCHCOC_6H_5 \\ \text{XII} \end{array}$$

Since these primary products can combine both with alpha,beta-unsaturated ketones and with carbonyl compounds it is apparent that in the case of those unsaturated ketones and esters which form both 1,4 and 1,2 addition products, the secondary reactions may become very complicated. These complications, however, occur but seldom because the primary addition products are far less reactive than Grignard reagents. Thus the

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(3) Kohler and Reimer, Am. *Chem J.*, 33, 333 (1905).

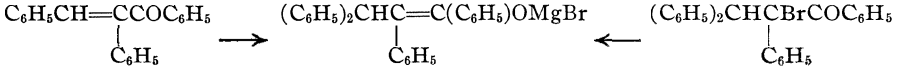
magnesium derivative which so readily combined with benzal acetophenone, showed little ability to react with methyl cinnamate and none at all to combine with acetone, cyclohexanone or methyl benzoate.

Complications of an entirely different kind, however, frequently arise when one equivalent of an unsaturated ketone is added to a Grignard reagent in the usual manner. Owing to the difference in the speeds of the primary and secondary reactions, the latter usually does not become significant until approximately half a mole of the ketone has been added. At that stage the solution contains three magnesium derivatives such as, for example

$$C_6H_5MgBr \quad (C_6H_5)_2CHCH{=}\underset{\underset{OMgBr}{|}}{C}C_6H_5 \qquad \begin{array}{l} C_6H_5CHCH{=}C(OMgBr)C_6H_5 \\ \quad\quad | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array}$$

The first two derivatives compete for any additional unsaturated ketone that is added but they are incapable of reacting with each other under any conditions. The third magnesium derivative, however, reacts with the Grignard reagent like any other saturated ketone. By the time all of the unsaturated ketone has been added, the solution contains primary, secondary and tertiary magnesium compounds that on hydrolysis yield a mixture which frequently cannot be separated and which at best gives a greatly diminished quantity of the primary product.

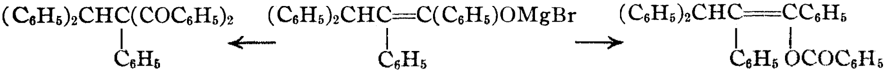
These complications can almost invariably be prevented by using a sufficient excess of Grignard reagent. Frequently they do not occur at all because the primary addition product is too sluggish to compete successfully with the Grignard reagent for the saturated ketone. The activity of these magnesium derivatives appears to depend largely on space relations, the addition products which are formed from ketones with a hydrocarbon residue in the alpha position being almost completely inert. Thus by allowing phenylmagnesium bromide to react either with benzal desoxybenzoin or with alpha bromo triphenylpropiophenone it is possible to make a magnesium derivative which differs from the one we have described only in that it has a phenyl group in the alpha position.



$$C_6H_5CH{=}\underset{\underset{C_6H_5}{|}}{C}COC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{C}{=}C(C_6H_5)OMgBr \longleftarrow (C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{C}BrCOC_6H_5$$

XIII

This new magnesium derivative is almost completely inactive. It cannot be carbonated, will not combine either with benzaldehyde or benzal acetophenone, and does not react with ethyl formate; it reacts only with acids, bromine, oxygen and acid chlorides. And the mechanism of the reaction with acid chlorides may be different from that of the simpler magnesium derivatives. Grignard reagents, as is well known, convert acid chlorides first into ketones and finally into the magnesium derivatives of tertiary alcohols. The magnesium derivatives which are obtained by adding Grignard reagents to alpha, beta-unsaturated ketones which have no substituent in the alpha position convert the same acid chlorides into the magnesium derivatives of diketones. The magnesium derivative under consideration likewise reacts with these same acid chlorides, but the products are esters.



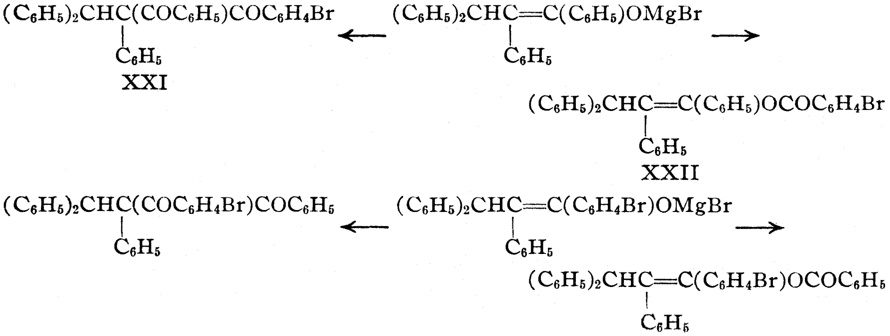
$$\begin{array}{ccccc} (C_6H_5)_2CHC(COC_6H_5)_2 & \longleftarrow & (C_6H_5)_2CHC{=}C(C_6H_5)OMgBr & \longrightarrow & (C_6H_5)_2CHC{=}CC_6H_5 \\ | & & | & & |\qquad | \\ C_6H_5 & & C_6H_5 & & C_6H_5\ OCOC_6H_5 \\ \text{XV} & & \text{XIV} & & \text{XVI} \end{array}$$

We suspected this difference in the direction of the reaction at the outset, because the melting points of the products obtained from acetyl and benzoyl chloride appeared to be too low for such a completely substituted diketone as is represented by XV. We were confirmed in this suspicion when we found that in the case of benzoyl chloride we obtained two isomeric products, both of which were rapidly hydrolyzed by methyl alcoholic solutions of potassium hydroxide too dilute to cleave beta diketones. But in order to prove the structure of these products conclusively it was necessary to compare products formed by introducing two different acyl groups in a different sequence. We therefore prepared the corresponding *p*-bromo compounds in a series of steps which is represented as follows

$$C_6H_5CH_2COCl \longrightarrow \underset{\text{XVII}}{C_6H_5CH_2COC_6H_4Br} \longrightarrow \underset{\text{XVIII}}{C_6H_5CHClCH(C_6H_5)COC_6H_4Br} \longrightarrow$$

$$\underset{\text{XIX}}{C_6H_5CH{=}C(C_6H_5)COC_6H_4Br} \longrightarrow \underset{\text{XX}}{(C_6H_5)_2CHC(C_6H_5){=}C(C_6H_4Br)OMgBr}$$

With this material in hand it was possible to settle the matter conclusively by means of the reactions which are represented by the following equations



$$\begin{array}{ccccc} (C_6H_5)_2CHC(COC_6H_5)COC_6H_4Br & \longleftarrow & (C_6H_5)_2CHC{=}C(C_6H_5)OMgBr & \longrightarrow & \\ | & & | & & \\ C_6H_5 & & C_6H_5 & & \\ \text{XXI} & & & & (C_6H_5)_2CHC{=}C(C_6H_5)OCOC_6H_4Br \\ & & & & | \\ & & & & C_6H_5 \\ & & & & \text{XXII} \end{array}$$

$$\begin{array}{ccccc} (C_6H_5)_2CHC(COC_6H_4Br)COC_6H_5 & \longleftarrow & (C_6H_5)_2CHC{=}C(C_6H_4Br)OMgBr & \longrightarrow & \\ | & & | & & \\ C_6H_5 & & C_6H_5 & & \\ & & & & (C_6H_5)_2CHC{=}C(C_6H_4Br)OCOC_6H_5 \\ & & & & | \\ & & & & C_6H_5 \\ & & & & \text{XXIIT} \end{array}$$

We found that the products of these reactions are different, the one being hydrolyzed to bromobenzoic acid and the bromine-free ketone, and the other to benzoic acid and the bromo ketone. The substances are, therefore, esters.

Experimental

I. Addition of the Magnesium Derivative of β,β-Diphenyl Propiophenone to Unsaturated Ketones

Preliminary experiments showed that in an atmosphere of nitrogen it is possible to convert a mole of α-bromo-β,β-diphenyl propiophenone completely into the magnesium derivative represented by (I) by means of a solution of phenylmagnesium bromide prepared from 1.1 atoms of magnesium. These proportions were therefore used in the following experiments.

Addition to Benzal Acetophenone, **β-Phenyl-γ-benzoyl-γ-benzhydryl Butyrophenone.** 111.—Fourteen and six-tenths grains of the bromo compound was added to a solution of phenylmagnesium bromide prepared from 1.06 g. of magnesium. Although sparingly soluble in ether, the bromo compound dissolved rapidly in the reagent. The solution was boiled for an hour, then treated with 8.33 g. of the unsaturated ketone. It immediately developed a deep orange color and it soon began to deposit a crystalline yellow magnesium derivative (II). It was stirred at the ordinary temperature for forty-five minutes and then filtered. The filtrate and half of the solid were treated separately with iced acid in the usual manner, and the rest of the solid with ammonia and ammonium chloride. All three portions gave the same product—a compound which separated from acetone and alcohol in small prismatic crystals and which melted at 180°.

Anal. Calcd. for $C_{36}H_{30}O_2$: M, 492; C, 87.5; H, 6.1. Found: M, 468; C, 87.7; H, 6.3.

The Mono-oxime, **IV.**—To a solution of 10 g. of the diketone in 1000 cc. of boiling alcohol were added 8.5 g. of hydroxylamine hydrochloride and 18 g. of potassium hydroxide. The solution was boiled for three hours, then distilled to small volume and diluted with water. The product was recrystallized from alcohol.

Anal. Calcd. for $C_{36}H_{31}O_2N$: C, 84.9; H, 6.1. Found: C, 85.4; H, 6.3.

The oxime is readily soluble in ether, moderately soluble in boiling alcohol. It separates from alcohol in stout needles or long prisms and it melts at 165°. In order to confirm its relation to the diketone, an alcoholic solution containing a small quantity of the oxime and a little concentrated hydrochloric acid was digested on a steam-bath and then diluted with water. The diketone was the only product.

Beckmann Rearrangement of the Oxime, **β-Phenyl-γ-benzoyl-γ-benzhydrylbutyric Anilide.** V.—To a solution of 5.5 g. of the oxime in 300 cc. of absolute ether 5.5 g. of phosphorus pentachloride was added in small portions. The mixture was boiled for twenty minutes, then concentrated to 150 cc., and gradually poured into ice water. The resulting gummy precipitate became granular when the ether was evaporated and the residue was digested on a steam-bath. The solid was recrystallized from alcohol.

Anal. Calcd. for $C_{36}H_{31}O_2N$: C, 84.9; H, 6.1. Found: C, 85.0; H, 6.4.

The anilide is sparingly soluble in ether, moderately soluble in boiling alcohol. It crystallizes in thin needles and it melts at 198". The yield was excellent.

Hydrolysis of the Anilide, **β-Phenyl-γ-benzoyl-γ-benzhydryl-butyric** Acid. **VI.**—The anilide is hydrolyzed with difficulty. An attempt to hydrolyze it by prolonged boiling with alcoholic potassium hydroxide failed completely, all of the anilide being recovered. It can be hydrolyzed by protracted heating to 180° with concd. hydrochloric acid, but owing to cleavage and other reactions, the yield is small—about 35%. It was finally hydrolyzed more successfully by heating it for eight hours to 180° with a solution of concd. hydrochloric acid in glacial acetic acid. The yield of acid was 60%. It crystallized from ether and petroleum ether in long slender needles and melted at 156°.

Anal. Calcd. for $C_{30}H_{26}O_3$: C, 83.0; H, 6.1. Found: C, 83.0; H, 6.3.

Bromination of the Acid, **β-Phenyl-γ-bromo-γ-benzoyl-butyric** Acid, **VII.**—Bromine was added, little by little, to a solution of the acid in chloroform until the color persisted. The solution was allowed to evaporate spontaneously; it gradually deposited a crystalline bromo acid and left an oily residue. The oil was removed with ether and petroleum ether, and distilled with steam. The distillate contained a precipitate which, after crystallization from ether, melted at 66° and which was identified as diphenylcarbinol by comparison with a sample on hand. One of the bromination products, therefore, was diphenylmethyl bromide.

The bromo acid was recrystallized from chloroform and petroleum ether. It separated in small prisms and it melted at 166°.

Anal. Calcd. for $C_{17}H_{15}O_3Br$: C, 58.8; H, 4.4; Br, 22.7. Found: C, 58.5; H, 4.5; Br, 22.4.

β-Phenyl-γ-benzoyl-butyro Lactone, VIII.—The lactone gradually separates as a crystalline precipitate when a clear solution of the bromo acid in the minimum quantity of dilute sodium carbonate is left to itself; but it is more easily obtained by warming a moist ethereal solution of the hydroxy acid with a little hydrogen chloride. It was purified by crystallization from ether and petroleum ether from which it separates in small cubes melting at 120°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.7; H, 5.4.

β-Phenyl-γ-hydroxy-γ-benzoyl-butyric Acid, $C_6H_5COCHOHCH(C_6H_5)CH_2COOH$, **IX.**—The hydroxy acid is very readily obtained by dissolving either the lactone or the bromo acid in excess of base and acidifying the solution. It was recrystallized from ether and petroleum ether from which it separated in colorless needles melting at 146°.

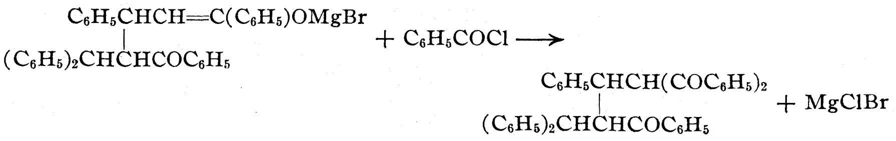
Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.6. Found: C, 71.6; H, 5.7.

Bromination of the Diketone.—Bromine was added in small quantities to a solution of 0.5 g. of the diketone in 20 cc. of chloroform until the color persisted. The solution was warmed for an hour, then concentrated and diluted with ether. As was to be expected, the product was a mixture of mono and dibromo compounds, but by repeated recrystallization from methyl alcohol it was possible to isolate a monobromo compound which melted at 132° and which was identified as α,γ-dibenzoyl-β-phenyl-γ-bromopropane, by comparison with a sample on hand. The yield was about 33%.

Action of Benzoyl Chloride on the Secondary Magnesium Derivative.—Although this magnesium derivative (II) does not combine either with more unsaturated ketone or with benzaldehyde, it still reacts with benzoyl chloride. An ethereal solution of 14.6 g. of α-bromo-β,β-diphenyl propiophenone was added to a solution of phenylmagnesium bromide prepared from 1.06 g. of magnesium. After this solution had been boiled for twenty minutes, it was treated with 8.33 g. of benzal acetophenone and boiled for four hours during which the usual yellow magnesium derivative was deposited. Finally 7 g. of benzoyl chloride was added and the mixture was boiled again until the yellow magnesium derivative was completely replaced by a colorless crystalline precipitate. The excess of benzoyl chloride was removed with sodium carbonate and the organic product purified by recrystallization from benzene. It separated in silky needles and melted at 180°. The yield was 17.5 g.

Anal. Calcd. for $C_{43}H_{34}O_3$: C, 86.4; H, 5.7. Found: C, 86.5; H, 6.0.

The composition shows that the reaction introduces an additional benzoyl group. In all probability the substance is a triketone formed in accordance with the equation



$$\begin{array}{l} C_6H_5CHCH{=}C(C_6H_5)OMgBr \\ \qquad\quad | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array} + C_6H_5COCl \longrightarrow \begin{array}{l} C_6H_5CHCH(COC_6H_5)_2 \\ \qquad\quad | \\ (C_6H_5)_2CHCHCOC_6H_5 \end{array} + MgClBr$$

Thus it was not hydrolyzed even when it was boiled with a solution of potassium hydroxide in methyl alcohol which rapidly hydrolyzed all the benzoates encountered in this work in the cold. It therefore is not a benzoate but thus far its structure has not been established with certainty.

Addition to **Benzalacetone, α-Benzhydryl-β-phenyl-γ-acetyl** Butyrophenone, $\mathrm{CH_3COCH_2CH(C_6H_5)CH[CH(C_6H_5)_2]COC_6H_5}$.—The reaction was carried out in the same manner as with benzal acetophenone and the substances were used in the same proportions. The product was an oily mixture from which it was difficult to separate a definite compound, and the amount of solid ultimately isolated was small. The solid crystallized from ether–petroleum ether in transparent prisms and melted at 153°.

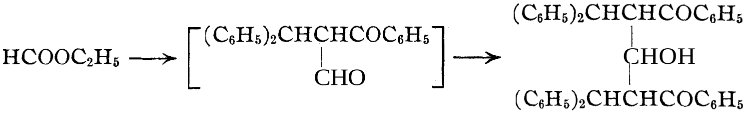
Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.1; H, 6.5. Found: C, 85.9; H, 6.7.

II. Reaction of the Magnesium Derivative of Diphenyl Propiophenone with Aldehydes and Esters

As indicated in the introduction, the magnesium derivative reacts with aldehydes but not with ketones; with ethyl formate but not with more complex esters. The structure of the products of these reactions was established with comparative ease. The product from benzaldehyde reacted with two moles of methylmagnesium iodide and liberated one mole of methane, showing that it contained both an hydroxyl and a carbonyl group. In all probability, therefore, it had been formed by the addition of the magnesium derivative to the carbonyl group of the aldehyde—a fact which was definitely established by oxidizing the substance to benzhydryl dibenzoyl methane

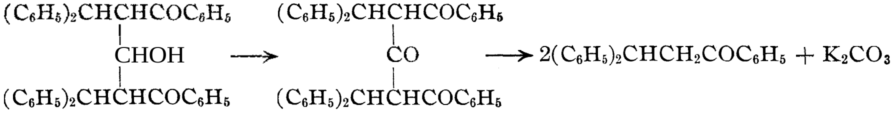
$$\mathrm{(C_6H_5)_2CHCH(COC_6H_5)CHOHC_6H_5} \longrightarrow \mathrm{(C_6H_5)_2CHCH(COC_6H_5)_2}$$

The composition of the product from ethyl formate showed that it had been formed from two molecules of the magnesium derivative and one of the ester. It was *a priori* probable, therefore, that the reaction had followed the same course as with benzaldehyde, the ester being in effect and the intermediate in reality an aldehyde



$$\mathrm{HCOOC_2H_5} \longrightarrow \left[\begin{array}{c}\mathrm{(C_6H_5)_2CHCHCOC_6H_5}\\ |\\ \mathrm{CHO}\end{array}\right] \longrightarrow \begin{array}{c}\mathrm{(C_6H_5)_2CHCHCOC_6H_5}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(C_6H_5)_2CHCHCOC_6H_5}\end{array}$$

By cautious treatment with chromic acid it was possible to oxidize the product to a triketone, which alkalies cleaved quantitatively to carbonate and two molecules of diphenyl propiophenone



$$\begin{array}{c}\mathrm{(C_6H_5)_2CHCHCOC_6H_5}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(C_6H_5)_2CHCHCOC_6H_5}\end{array} \longrightarrow \begin{array}{c}\mathrm{(C_6H_5)_2CHCHCOC_6H_5}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{(C_6H_5)_2CHCHCOC_6H_5}\end{array} \longrightarrow \mathrm{2(C_6H_5)_2CHCH_2COC_6H_5} + \mathrm{K_2CO_3}$$

Addition to Benzaldehyde. **α-Phenyl-β-benzoyl-γ,γ-diphenyl Propanol.** XI.—A solution of 4 g. of benzaldehyde in an equal volume of ether was added gradually to a solution of the magnesium derivative which had been prepared in the usual manner from 14.6 g. of the bromo compound. The mixture was boiled for four hours during which it gradually turned to a thick paste. By decomposition with iced acid and the usual manipulations this paste was converted into a solid. The solid was purified by crystallization from acetone and methyl alcohol. It separated in needles and it melted at 133°. The yield was 77%.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 85.7; H, 6.1. Found: C, 85.5; H, 6.2.

Oxidation.—A solution of 0.75 g. of chromic acid in the minimum quantity of water was added gradually to a warm solution of one gram of the alcohol in 35 cc. of glacial acetic acid. The solution was warmed on a steam-bath until the color changed to green, then allowed to cool. It deposited 0.68 g. of fine needles which melted at 225°, and were identified as benzhydryl dibenzoyl methane by comparison with a sample on hand.

Reaction with Ethyl Formate, α,γ-Dibenzoyl-α,γ-dibenzhydryl-β-hydroxy Propane. XII.—One and one-half grams of ethyl formate was added to a solution of the magnesium derivative which had been prepared from 14.6 g. of the bromo compound. A white precipitate formed immediately but the mixture was boiled for forty-five minutes before it was decomposed with ice and acid in the usual manner. The product was recrystallized from benzene from which it separated in thin needles which melted at 202". The yield was quantitative.

Anal. Calcd. for $C_{43}H_{36}O_3$: C, 86.0; H, 6.0. Found: C, 85.9; H, 6.0.

Oxidation, α,γ-Dibenzoyl-α,γ-dibenzhydryl Acetone.—A solution of 0.12 g. of chromic acid in acetic acid was added to a solution of one gram of the hydroxyl compound in 150 cc. of hot glacial acetic acid. The color changed immediately and when the solution was diluted with a little water and cooled it deposited 0.75 g. of the triketone. The substance was purified by recrystallization from glacial acetic acid from which it separated in needles melting at 232°.

Anal. Calcd. for $C_{43}H_{34}O_3$: C, 86.0; H, 5.7. Found: C, 86.0; H, 5.7.

Cleavage of the Triketone.—A solution of 0.4 g. of the oxidation product in 10% alcoholic potassium hydroxide was boiled for nine hours, then diluted with water and extracted with ether. The ethereal extract, on evaporation, left pure β,β-diphenyl propiophenone.

III. Experiments with the Magnesium Derivative of α,β,β-Triphenyl Propiophenone

The magnesium derivative was prepared in ethereal solution by the action of phenylmagnesium bromide on the alpha bromo derivative of the ketone or on benzal desoxybenzoin. Attempts to add it to benzal acetophenone, benzaldehyde and formic ester were unsuccessful. In each case, after prolonged boiling, hydrolysis resulted only in the bromine-free ketone.

Reaction with Benzoyl Chloride, α,β,γ,γ-Tetraphenylpropenyl Benzoate, XVI.—An ethereal solution of 8.8 g. of the bromo compound was added to a solution of phenylmagnesium bromide prepared from 0.52 g. of magnesium. The mixture was boiled for forty-five minutes, then treated with 3.0 g. of benzoyl chloride, boiled for another hour and hydrolyzed with iced acid. The product was crystallized from ether and methyl alcohol. It separated in cubical crystals and it melted at 110°. It is very readily soluble in ether, sparingly soluble in methyl alcohol. The yield was 7.2 g.

Anal. Calcd. for $C_{34}H_{26}O_2$: M, 466; C, 87.5; H, 5.5. Found: M, 447; C, 87.5; H, 5.5.

In a subsequent experiment 9.5 g. of benzal desoxybenzoin was added to a solution of phenylmagnesium bromide prepared from 0.8 g. of magnesium. The mixture was boiled for twenty-five minutes, then treated with 5.7 g. of benzoyl chloride and boiled for two hours. In this case the usual manipulation resulted in a mixture composed of the benzoate melting at 110° and a stereoisomeric benzoate melting at 131°. The substance was purified by recrystallization from methyl alcohol, in which it is sparingly soluble and from which it separated in needles. The isomers were formed in approximately equal amounts, the yield of the higher melting compound being 7.5 g.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.5; H, 5.5. Found: C, 87.6; H, 5.8.

Hydrolysis of the Benzoates.—Half a gram of each benzoate was dissolved in the minimum quantity of boiling absolute methyl alcohol. To each solution enough methyl alcoholic potassium hydroxide was added to make the concentration of the base 0.2%. The solutions were then set aside without further heating. Triphenyl propiophenone began to crystallize as the solutions became cool. In a few hours both solutions were allowed to evaporate to complete dryness in a current of air. From the residue, water extracted sodium benzoate, and left pure ketone. The yield was quantitative.

***p*-Bromodesoxybenzoin. XVII.**—To a solution of 77 g. of phenyl acetyl chloride in 150 cc. of bromobenzene was added, in small portions and with constant stirring, 65 g. of powdered aluminum chloride. The mixture was stirred for a day at the ordinary temperature, then left to itself for twenty-four hours before it was decomposed with ice and concentrated hydrochloric acid. Distillation with steam removed the excess of bromobenzene and left an orange colored paste which showed no tendency to solidify and which therefore was distilled under diminished pressure. The first fraction, boiling at 160–200° (12 mm.), solidified on cooling. Recrystallization of the solid from methyl alcohol gave 58 g. of a product which crystallized in needles and melted at 115°.

Anal. Calcd. for $C_{14}H_{11}OBr$: C, 61.1; H, 4.0. Found: C, 61.2; H, 4.1.

α,β-Diphenyl-β-chloro *p*-Bromopropiophenone. XVIII.—A solution of 30 g. of ***fi***-bromodesoxybenzoin in 60 g. of benzaldehyde was saturated with dry hydrogen chloride, then kept at 0° for ten hours in a slow current of the gas. The resulting solid was collected on a filter, washed with ether and petroleum ether and recrystallized from alcohol. It separated in needles which melted at 171°.

Anal. Calcd. for $C_{21}H_{16}OClBr$: C, 63.1; H, 4.0. Found: C, 63.1; H, 4.2.

Benzal *p*-Bromodesoxybenzoin, XIX.—A solution of 30 g. of the chloro compound in 500 cc. of methyl alcohol containing one equivalent of potassium acetate and slightly less than one equivalent of sodium carbonate was boiled for four hours. Most of the solvent was then removed by distillation. The residue, on cautious dilution with water, deposited a crystalline solid which crystallized from ether in large prisms, and which melted at 105°.

Anal. Calcd. for $C_{21}H_{15}OBr$: C, 69.4; H, 4.1. Found: C. 69.5; H, 4.3.

α-(*p*-Bromophenyl)-β-benzhydryl-β-phenyl-ethenyl Benzoate. XXIII.—An ethereal solution of benzal *p*-bromo desoxybenzoin was added to a solution of phenylmagnesium bromide prepared from 1.2 g. of magnesium. The mixture was boiled for twenty minutes, then treated with 7.5 g. of benzoyl chloride and boiled for two hours more. The usual decomposition with iced acid gave an oil which contained benzoyl chloride. An ethereal solution of the oil was freed from benzoyl chloride by shaking with sodium carbonate, then dried, concentrated and diluted with petroleum ether. It deposited a solid which crystallized in small lustrous prisms and melted at 144'.

Anal. Calcd. for $C_{33}H_{25}O_2Br$: C, 74.8; H, 4.6. Found: C. 74.7; H. 4.8.

Hydrolysis, α,β,β-Triphenyl-*p*-bromo Propiophenone $(C_6H_5)_2CHCH(C_6H_5)COC_6H_4Br$.—The hydrolysis was carried out in exactly the same manner as that of the bromine-free benzoates. The crude product melted at 200° and the melting point was not changed by recrystallization from acetone and methyl alcohol from which the bromo ketone crystallized in large lustrous needles. The aqueous extract of the residue, that was left after the evaporation of the mother liquors, contained only sodium benzoate.

Anal. Calcd. for $C_{27}H_{21}OBr$: C, 73 5; H, 4.8. Found: C, 73.4; H, 4.9.

α,β-Diphenyl-β-benzhydryl-ethenyl *p*-Bromobenzoate. XXII.—To a solution of phenylmagnesium bromide from 0.8 g. of magnesium was added 8.4 g. of finely powdered benzal desoxybenzoin. The mixture was boiled for twenty minutes, then treated with 7.5 g. of freshly distilled *p*-bromobenzoyl chloride and boiled again for two hours. The usual manipulations gave a product which was sparingly soluble in ether and in alcohol, which crystallized in prisms, and which melted at 183°.

Anal. Calcd. for $C_{34}H_{25}O_2Br$: C, 74.8; H, 4.6. Found: C, 74.7; H, 4.7.

Hydrolysis.—The ester on hydrolysis with dilute methyl alcoholic potassium hydroxide gave but two products: triphenyl propiophenone and p-bromobenzoic acid.

Summary

1. The magnesium derivatives which are formed by the addition of Grignard reagents to those α,β-unsaturated ketones which have no substituents in the alpha position behave like the enolates of 8-ketonic esters; like these enolates they combine with unsaturated ketones and with other substances that have sufficiently active carbonyl groups. The reaction with acid chlorides results in the formation of C-acyl derivatives.

2. The magnesium derivatives which are formed by adding Grignard reagents to α,β-unsaturated ketones which have hydrocarbon residues in the alpha position, combine neither with unsaturated ketones nor with aldehydes; they therefore do not form secondary products. The reaction between these magnesium derivatives and acid chlorides results in the formation of O-acyl derivatives.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Furan Reactions. IV. Furoic Acid from Furfural

BY CHARLES D. HURD, J. W. GARRETT[1] AND E. N. OSBORNE[1]

In the Cannizzaro reaction with furfural, mineral acids cannot be used to neutralize the excess of alkali without resinifying the furfuryl alcohol which is formed. Hence, it is customary[2] to extract the latter with ether before acidification. In the method proposed, the excess of alkali is neutralized with furoic acid and the furfuryl alcohol separated directly, thus making the method suitable for large scale use. Also, the excess of alkali may be omitted altogether with yields only slightly lower.

The direct oxidation of furfural to furoic acid by means of potassium dichromate and sulfuric acid has also been studied and a satisfactory method developed. The manganous salt of furoic acid was synthesized. It was found to crystallize with three molecules of water.

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(1) Holders of Quaker Oats Fellowships, administered through the Miner Laboratories, Chicago.

(2) Wilson, "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 44.

Experimental Part

The Cannizzaro Reaction.—Following the direction of "Organic Syntheses,"[2] 1 kg. (10.4 moles) of redistilled furfural and 820 g. of 33% sodium hydroxide solution (6.9 moles of sodium hydroxide) were used to bring about the Cannizzaro reaction. To remove the excess 1.7 moles of alkali at the conclusion of the reaction, 1.8 moles (200 g.) of furoic acid[3] was added directly to the mixture and the mass stirred well. The mixture was cooled to 0° and pressed as dry as possible on a suction filter. The solid was transferred to a beaker, triturated therein with a 200–250 cc. portion of cold water, cooled to −5° and again sucked dry. The trituration of the solid with water was repeated.

The combined filtrates were distilled at 25 mm. nearly to dryness using a heating bath, the temperature of which wss kept below 145°. Water was removed from this distillate by vacuum distillation from a special Claisen flask equipped with a water-cooled head.[4] When the water had been distilled away, the residue of furfuryl alcohol was thrice shaken with saturated sodium bisulfite solution to remove any furfural present. The furfuryl alcohol was fractionated under reduced pressure (83° at 24 mm.); yield, 367–390 g., or 72–76%. The refractive index, n^{21}_{D}, was 1.4869.

All the solid residues were dissolved in warm water and filtered from a small amount of dark, insoluble material. The filtrate was acidified with concd. hydrochloric acid, cooled to 0° and filtered. The solid was washed twice with a little ice water and then dried. Yields of 420–440 g. (73–76%) of white furoic acid were obtained in excess of the 200 g. which was also recovered. The ash content of the furoic acid in this stage of purity was 1.5%, weighed as the sulfate.

If a slight deficiency of alkali was used at the outset (5.0 moles of sodium hydroxide for each 10.4 moles of furfural), good results were obtained also. In this case the reaction mixture was filtered and worked up directly without adding any furoic acid. Otherwise an identical procedure was followed. The yields of furfuryl alcohol were about the same as the above, whereas the yields of furoic acid were about 5% less.[5]

Manganous Furoate Trihydrate, $(C_4H_3O—COO)_2Mn\cdot 3H_2O$.—Twenty-eight grams (0.25 mole) of furoic acid was dissolved in a minimum quantity of hot water (about 125 cc.) and then 15 g. (0.13 mole) of solid manganous carbonate was added slowly. The mixture was stirred and heated until the evolution of carbon dioxide had ceased. The slight excess of manganous carbonate was filtered off and the filtrate was concentrated to a thick sirup which possessed a light brown color. When cool, crystallization was induced by scratching. The dark pink crystals weighed 23.6 g.; yield, 68.1%.

The product was dissolved in a small portion of hot water. Slow evaporation at about 50° with seeding gave large crystals. The sample used for determination of water of crystallization was dried in a desiccator over calcium chloride. Then the water was driven off at 105°. In the analysis for manganese, the sample was dried for three hours at 105° to constant weight.

Anal. Subs., 1.9712; H_2O, 0.3173. Calcd. for $(C_4H_3O—COO)_2Mn\cdot 3H_2O$: H_2O, 16.33. Found: H_2O, 16.20. Subs., 0.6535: Mn_3O_4, 0.1790. Calcd. for $(C_4H_3O—COO)_2Mn$: Mn, 19.81. Found: Mn, 19.73.

Manganous furoate was found to be very soluble in hot and cold water, soluble in ordinary ethyl alcohol, insoluble in absolute alcohol, carbon tetrachloride and acetone. The anhydrous salt begins to decompose at about 290°.

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(3) It was found that ammonium sulfate could also be used satisfactorily in this neutralization.

(4) This was of the Clarke and Rahrs type [*Ind. Eng. Chem.*, 15, 349 (1923)] but any efficient column would be satisfactory.

(5) From experiments with Mr. W. A. Whittier. Dr. F. N. Peters, Jr., of the Quaker Oats Co. Chemical Laboratory has found this method suitable for runs nine times the size of the one described. He recommended a combination of salting-out (by sodium chloride) and distillation rather than distillation alone to remove the furfuryl alcohol from its aqueous solution.

Oxidation of Furfural.—After several experiments with temperature and time and dilution as the variables, the following conditions seemed to give the best yields in this oxidation.

In a round-bottomed liter flask which was equipped with a mechanical stirrer, dropping funnel and reflux condenser, were placed 100 g. of furfural, 100 g of potassium dichromate and 10 g. of water. The flask was then heated to 100° on a steam-bath and, dropwise, there was added a mixture of 200 g. of sulfuric acid and 100 g. of water during thirty to forty-five minutes. The heat of reaction was such that the steam-bath was removed after a short time. When complete, the reaction mixture was cooled and nearly neutralized with sodium hydroxide. Then it was completely neutralized with sodium carbonate. The chromium hydroxide which was filtered off weighed 56 g. after drying. The filtrate was made acid with sulfuric acid and the dark brown precipitate of furoic acid was collected upon a filter. The filtrate was concentrated for more furoic acid. In all, 105 g. of crude material was formed. It was dissolved in the minimum amount of hot water, filtered from any insoluble matter, and the filtrate cooled. Eighty-seven grams (dry) of white furoic acid separated: yield, 75% The crystals melted at 131.5°.

Summary

A method is given for the oxidation of furfural to furoic acid by potassium dichromate and sulfuric acid. Improved directions are recorded for the preparation of furfuryl alcohol and furoic acid from furfural by the Cannizzaro reaction. Manganous furoate trihydrate is described.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDGBASTON, BIRMINGHAM, ENGLAND]

Sucrose and Other Disaccharides. Sir James Irvine's "Correction"

BY H. C. CARRINGTON, W. N. HAWORTH AND E. L. HIRST

In a recent paper which deals with the properties of 2,3,6-trimethylglucose and their bearing on the chemistry of the di- andpoly saccharides, Irvine and McGlynn[1] revert to a theme which was initiated and decided by one of us, but in their treatment of the subject they again dispense with the isolation of crystalline reference substances. They describe 2,3,6-trimethyl-γ-gluconolactone as a liquid with an initial rotation, $[\alpha]_D$ +80.5° or 90.5' (both values being given), observed in a mixture of alcohol and water of unspecified composition. As shown in our experimental section the pure lactone is a crystalline substance, m. p. 29–30°, with the initial rotation $[\alpha]_D$ +55° in water, alcohol or mixtures of the two solvents. We have characterized it as a γ-lactone by measuring its rate of mutarotation in water (which Irvine and McGlynn omitted to attempt), by preparing from it the crystalline phenylhydrazide of 2,3,6-trimethylgluconic

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[1] Irvine and McGlynn, THIS JOURNAL, 54, 356 (1932).

acid and by converting it by methylation into tetramethyl-γ-gluconolactone (characterized by the crystalline phenylhydrazide). It is prepared from 2,3,6-trimethylglucose which undergoes oxidative degradation to *d*-dimethoxysuccinic acid recognized as the crystalline methylamide.

This trimethyl-y-gluconolactone is obtainable by oxidation of 2,3,6-trimethylglucose both in the presence of hydrobromic acid and when the reaction is carried out in the presence of calcium carbonate. Under the latter conditions Irvine and McGlynn claim categorically that the oxidation product does not pass through the stage of the calcium salt. On frequent occasions we have made use of this procedure to obtain the calcium salt of the aldose sugar acids. So far from our criticism[2] of his experimental methods being, as he asserts, pointless we now publish experimental observations which show (a) that when the oxidation is conducted for eight hours at 0° at least 66% of the product is in the form of the calcium salt, (b) that an aqueous solution of the more stable γ-lactone of 2,3,6-trimethylgluconic acid reacts during five hours to the extent of 40% with calcium carbonate at 0°, (c) that the hydrolysis of the y-lactone to acid is greatly accelerated by hydrobromic acid.

The position is therefore that Irvine and McGlynn have completely misconceived the nature of the y-lactone, and on the basis of a sirupy product which bears no relation in properties to the pure substance it is claimed to be, they suggest that previous, but unspecified, results have a doubtful validity. Moreover, under the experimental conditions adopted by these authors, any lactone (γ or 6) formed by direct oxidation of the sugar must either hydrolyze to a mixture of acid and the two lactones or must be converted largely into the calcium salt. In these circumstances their experimental results can provide no sanction for any conclusions concerning the direct oxidation of 2,3,6-trimethylglucose to either the γ- or 6-lactone. Results have now been obtained by Isbell and Hudson's method[3] which suggest that in a buffered solution direct oxidation to the 8-lactone occurs but, on keeping, this changes in water to the equilibrium of y- and 6-lactone and free acid or salt. We are unable to see in what manner Irvine and McGlynn's oxidation experiments, coupled with a confirmation of earlier work by others on 2,3,6-trimethyl-γ-methylglucoside, can be used to substantiate the claim that "much further work and the application of new methods are alike necessary before definite constitutions can be assigned to the disaccharides and polysaccharides which are convertible into 2,3,6-trimethylglucose." Further work and new methods can only be welcomed but these authors overlook the fact that the actual terms they use in referring to five- and six-atom ring forms of 2,3,6-trimethylglucose are based on our original determination of the structure of γ- and normal sugars. As one of us has pointed out, new methods of

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(2) Hirst. THIS JOURNAL, 54, 2559 (1932).

(3) Isbell and Hudson, *J. Bur. Standards*, 8, 327 (1932).

attack were developed six years ago and definite constitutions have been assigned by these means to maltose, lactose, cellobiose, melibiose, 4-glucosidomannose and 4-galactosidomannose. In his recent letter[4] Sir James Irvine admits knowledge of these results but gives no reason for his omission to mention them and to state his objection either to the methods or to the formulas assigned.

Heptamethylsucrose.—In the isolation of tetramethyl-γ-fructose as a residue from methylated sucrose a partly methylated product was employed in which the whole of the hydroxyl groups of the fructose component were protected while the hydroxyl groups in the glucose portion were only partly methylated. On hydrolysis this led to the separation of a distillate consisting essentially of the desired fructose portion of sucrose, and the procedure was improved in subsequent papers.[5]

In the first paper dealing with the isolation of tetramethyl-γ-fructose,[6] the partly methylated sucrose, described as heptamethylsucrose, was considered to be a homogeneous substance but this view was corrected in a later paper,[7] wherein it was stated that heptamethylsucrose gives rise to "a mixture of trimethylglucoses and tetramethyl-γ-fructose," since we isolated both 2,3,6- and 2,4,6-trimethylglucoses from the glucose residues.

Sir James Irvine in his criticism[8] seems to be unaware of these facts since he occupies much space in attacking the earlier view of the homogeneity of heptamethylsucrose. His further statement that he was unable to obtain by fractional distillation a product which "consists essentially of heptamethylsucrose" can be dismissed briefly. He claims that it is impossible to isolate a product containing less than 30% of the octamethylsucrose and a compensating quantity of hexamethyl and lower methylated sucroses. Over a large and extended series of preparations of this material, and by repeated fractional distillation controlled by refractive indices of the fractions, we have experienced no difficulty in obtaining a product which is "essentially heptamethylsucrose" containing less than 2% of the octamethyl derivative. The yield of the desired product is subject to the original statement on such methylation processes, namely, that "the success of the operation is governed to a remarkable degree by the conditions of the experiment."[9] A specific warning against the use of octamethylsucrose is given in the paper by Avery, Haworth and Hirst.[5]

In the past nine years during which we have revised the constitutional formulas of all sugars we have repeatedly stated that no structure is acceptable unless it is based on the isolation of well-recognized crystalline substances. Despite the dangers involved in the non-observance of this

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(4) Irvine, THIS JOURNAL, 84, 2567 (1932).

(5) Avery, Haworth and Hirst, *J. Chem. Soc.*, 2308 (1927).

(6) Haworth, *ibid.*, 117, 206 (1920).

(7) Haworth and Sedgwick, ibid., 2574 (1926).

(8) Irvine, THIS JOURNAL, 54, 1486 (1932).

(9) Haworth, *J. Chem. Soc*, **107**, 9 (1915).

rule, Sir James Irvine persists in advancing conjectural formulas of sirupy products, and in this paper now under review he claims to have recognized a 2,3,5-trimethylglucose as a partly methylated hydrolysis product of methylated sucrose, and on this basis seeks to maintain "the disquieting possibility that methylation is accompanied to some extent by a change in the position of the internal oxygen ring in a sugar."

In the present case he has neglected to take into account the application of partition coefficients, since he claims that tetra- and tri-substituted methylglucoses, each of which is soluble in chloroform, can be extracted by this solvent from aqueous solution by methods which allow of a "sharp separation" in that all the tri-substituted sugar remains in the water while the tetra- is extracted by chloroform. We have long known the contrary to be true. But in order to test the special case involved in this claim we have prepared 2,3-dimethylmethylglucoside which Sir James Irvine definitely identified in his product (owing to incomplete fractionation of his methylated sucrose), and we have shown that, after eight extractions from an 8% aqueous solution, more than 80% is taken up by the chloroform. This glucose derivative he has characterized by the conversion of its 6-p-toluenesulfonyl derivative into the 6-iodo compound. The supposed 2,3,5-trimethylglucose (obtained through the γ-methylglucoside) he also claims to have recognized by treating a residual mixture of 5 g. of a trimethyl-γ-methylglucoside-*p*-toluene sulfonate with sodium iodide in acetone, heating the product in acetonitrile solution with silver nitrate and weighing the silver iodide formed. By this means he calculates that the mixture contained 14% of a 6-p-toluenesulfonyl derivative (equal to 0.35 g. of the free sugar from 100 g. methylated sucrose). Inasmuch as the trimethylmethylglucosides were extracted by chloroform from water they must have contained some 2,3-dimethylmethylglucosides, and it is clear that the latter would also give a 6-p-toluenesulfonyl derivative which must react with sodium iodide. An amount of 0.35 g. of dimethylmethylglucoside, forming part of 17 g. of a sirupy mixture of "trimethylmethylglucosides" would not be revealed by C and H and OMe estimations (no analyses are quoted). The evidence therefore for the presence of 2,3,5-trimethylglucose (which alternatively he considers as possibly 1,3,4-trimethylfructose) is unacceptable. It is on this experimental basis that Sir James Irvine seeks to establish a claim that "the case now presented opens up grave possibilities" of the insecurity of carbohydrate formulas which we have established.

Experimental

2,3,6-Trimethyl-γ-gluconolactone.—Bromine (10 cc.) was added slowly to a solution of 2,3,6-trimethylglucose, m. p. 121°, (7 g.) in water (30 cc.) maintained at 35° After twenty-four hours the excess of bromine was removed by aeration and the solution was extracted with chloroform. Removal of the chloroform under diminished pressure left a yellow sirup which on distillation gave 2,3,6-trimethyl-γ-gluconolactone

(6.1 g.) as a colorless sirup which rapidly crystallized. Recrystallization from ether-light petroleum at −10° gave needles, m. p. 29–30°, b. p. about 130° (0.05 mm.), $n_{\mathrm{D}}^{16^\circ}$ 1.4625 (superfused solid), $[\alpha]_{\mathrm{D}}^{18}$ +55° in water, *c* 2.4; +56° in alcohol, *c* 0.5; +55° in 50% aqueous alcohol, c 0.4. 0.3193 g. of substance required 14.7 cc. of *N*/10 NaOH. Calcd. 14.5 cc. (Found: C, 49.0; H, 7.6; OMe, 41.2. $C_9H_{16}O_6$ requires C, 49.1; H, 7.3; OMe, 42.3%).

Under the conditions given by Irvine and McGlynn (eight hours at 0°) the oxidation is incomplete. The mixture (yield 50%) of sugar and lactone so obtained reduced Fehling's solution vigorously and when kept crystallized partially giving 2,3,6-trimethyl-γ-gluconolactone, m. p. 28°, identical with the material described above (yield 25%).

The rate of mutarotation of the 2,3,6-trimethyl-γ-gluconolactone in aqueous solution was similar to that of tetramethyl γ-gluconolactone: $[\alpha]_{\mathrm{D}}^{18^\circ}$ +55° initial value in water, *c* 2.4; 53° (12 hrs.); 52° (24 hrs.); 49° (60 hrs.); 46° (100 hrs.); 42° (200 hrs.); 40° (250 hrs.); 37° (500 hrs.); 37.5" (700 hrs.). After 700 hours the rotation fell extremely slowly. The rate of mutarotation was greatly accelerated by hydrobromic acid: $[\alpha]_{\mathrm{D}}^{19^\circ}$ +55°, initial value in *N* aqueous HBr, c 0.5; 54° (3 min.); 52° (15 min.); 48° (30 min.), 44" (1 hr.); 42" (3 hrs.); 40° (5 hrs.); 34" (48 hrs.).

The rotation of the acid in water was $[\alpha]_{\mathrm{D}}^{20^\circ}$ +28° initial value, *c* 1.4 (calcd. as lactone); 30° (15 min.); 31° (45 min.); 32° (90 min.); 32.5° (200 min.; constant value, observed for 70 hrs.). The proportions of δ-lactone, y-lactone and acid at equilibrium cannot be calculated from these figures, but the proportion of acid must be at least 85% since, as shown below, the 8-lactone has a rotation higher than 55°.

The phenylhydrazide of 2,3,6-trimethylgluconic acid was prepared by heating on the water-bath a mixture of the lactone with a slight excess of phenylhydrazine After ten minutes the mixture solidified. The excess of phenylhydrazine was removed by washing with benzene and the product was recrystallized from ethyl acetate, giving colorless needles, m. p. 145°, yield 90%. (Found: C, 55.0; H, 7.4; N, 8.8; OMe, 28.2. $C_{15}H_{24}O_6N_2$ requires C, 54.9; H, 7.3; N, 8.6; OMe, 28.4%)

On methylation with methyl iodide and silver oxide 2,3,6-trimethyl-γ-gluconolactone gave 2,3,5,6-tetramethyl-γ-gluconolactone recognized as the corresponding crystalline phenylhydrazide, m. p. 136°, alone or when mixed with an authentic sample.

Oxidation of 2,3,6-Trimethylglucose in the presence of Calcium Carbonate.—When the oxidation of 2,3,6-trimethylglucose was carried out at 0° in the presence of calcium carbonate most of the product passed through the stage of the calcium salt (contrast Irvine)[4] 2,3,6-Trimethylglucose (1 g.) was oxidized for eight hours at 0° by bromine in the presence of calcium carbonate. The bromine was removed by aeration and the excess of calcium carbonate by filtration. Aliquot parts of the filtrate were analyzed for halogen and calcium. (Found: total calcium in solution, 0.250 g. Calcium equivalent to bromide ion in solution 0.186 g.). The excess calcium (0.064 g.) which existed as the calcium salt of an organic acid was equivalent to 0.77 g. of 2,3,6-trimethylgluconic acid; *i*. e., 66% of the theoretically possible quantity occurs as the calcium salt. Control experiments showed that this method of analysis is not vitiated by errors due to the formation of calcium bicarbonate. When 2.5 cc. of 0 135 N hydrobromic acid was added slowly over a period of one hour to a mixture of calcium carbonate and water at 0° the calcium in the filtered solution was found to be exactly equivalent to the added hydrobromic acid. The solution therefore contained no bicarbonate.

Again, when a solution of 2,3,6-trimethyl-γ-gluconolactone (0.150 g.) in water (10 cc.) was kept in contact with calcium carbonate at 0° for five hours the filtered solution contained 0.0054 g. of calcium (determined by precipitation as the oxalate and estimated volumetrically with permanganate). This is equivalent to the transformation of 0.059 g. of trimethyl-γ-gluconolactone into the calcium salt. The stable y-lactone is converted into the calcium salt to the extent of 40% under these mild conditions

Oxidation by **Isbell and** Hudson's Method.—When 2,3,6-trimethylglucose was oxidized in a buffered solution in accordance with Isbell and Hudson's procedure[3] the following observations were made: $[\alpha]^{20°}_{D}$ +60° in a solution (24 cc.) containing sodium acetate (3.75 g.), glacial acetic acid (0.25 cc.), trimethylglucose (2.5 g.). Five minutes after the addition of bromine (0.75 cc.) the $[\alpha]_D$ was 4-73'; 70° (10 min.); 63" (20 min.); 55° (45 min.); 53° (60 min.); 49° (90 min.); 43° (300 min.). After eleven minutes a sample of the solution was removed, and the bromine eliminated by shaking with olive oil. The solution then had $[\alpha]^{20°}_{D}$ +49° (50 min. after commencement of oxidation); 48° (90 min.); 46° (300 min.). At eleven minutes it was found that the oxidation was complete to the extent of 50%. Since the rotation of the y-lactone is +55°, the above figures indicate that under these conditions preferential formation of the δ-lactone takes place.

Lactonization of **2,3,6-Trimethylgluconic** Acid.—The conditions governing the lactonization of 2,3,6-trimethylgluconic acid were complex. The pure γ-lactone was obtained invariably (a) by evaporating to a sirup an aqueous solution of the free acid containing a trace of mineral acid, (b) by evaporating a chloroform extract of an aqueous solution of the free acid to which some mineral acid had been added a short time previous to the extraction. Mixtures containing some δ-lactone in addition to 7-lactone were obtainable (a) by evaporating to a sirup of an aqueous solution of the y-lactone which had been kept at 100° for four hours, (h) from a chloroform extract of an aqueous solution of the free acid made immediately after liberation of the acid from a salt. Method (b) was uncertain in its results and sometimes gave pure y-lactone, particularly when the aqueous solution contained mineral acid. A typical experiment (method (a)) gave a mixture of lactones which had $[\alpha]^{17°}_{D}$ +61° initial value in water. *c* 0.4; 49° (3 hrs.); 49° (5 hrs.); 46° (17 hrs.); 41° (100 hrs.). The initial rapid fall in rotation followed by a slow fall is characteristic of a mixture of γ- and δ-lactones. Since the equilibrium rotation is +35° and that of the γ-lactone 4-55', an approximate value for the rotation of the IS-lactone can be calculated (+90°). The mixture with $[\alpha]_D$ +61° would therefore contain about 20% of the IS-lactone.

WITH C. W. LONG

Oxidation of **2,3,6-Trimethylglucose** by **Nitric** Acid.—Crystalline 2,3,6-trimethylglucose (5 g.) was heated on the water-bath (95°) for seven hours with nitric acid (40 cc., *d* 1.42) The acid was removed by distillation under diminished pressure, water being added from time to time. The sirupy product was boiled for six hours with 2% methyl alcoholic hydrogen chloride. The acid was removed by addition of silver carbonate and after removal of the solvent the esterified oxidation product was distilled giving 2.6 g., b. p. about 80° (0.05 mm.), n^{17}_{D} 1.4355, $[\alpha]^{17}_{D}$ +80° in water (*c* 1.7). This consisted almost entirely of methyl d-dimethoxysuccinate, as was proved by its conversion into the corresponding amide (yield 80%), m. p. 280° decomp., $[\alpha]^{17}_{D}$ 4-95' in water (*c* 0.4) and methylamide, m. p. 207–208°. A mixed melting point with an authentic sample of the methylamide prepared by Haworth and Jones[10] showed no depression. [Found (methylamide): C, 47.0; H, 7 9; N, 13 7. Calcd. for $C_8H_{16}O_4N_2$: C. 47.0; H, 7 85; N, 13.7%.] The yield of methyl d-dimethoxysuccinate was 80% of the theoretical.

Extraction of 2,3-Dimethyl-α-methylglucoside from Water by Chloroform.—A 4% aqueous solution of crystalline dimethyl-α-methylglucoside[11] was shaken with an equal volume of chloroform. On evaporation of the dried chloroform solution 4% of the original dimethyl-a-methylglucoside was recovered. Three successive extractions with an equal volume of chloroform removed 10% of the material in the aqueous solution. When a stronger aqueous solution (8%) was extracted thoroughly with chloro-

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[10] Haworth and Jones, *J. Chem. Soc.*, 2349 (1927).

[11] Irvine and Scott, *ibid.*, 103, 582 (1913).

form 85% of the 2,3-dimethylmethylglucoside was obtained in the chloroform extract. The solubility of the glucoside in chloroform is so marked that we have found extraction by chloroform of an aqueous solution (8–10% concentration) of the crude material a useful method of purification. (These experiments were carried out by Dr. A. C. Waine.)

Summary

The oxidation of 2,3,6-trimethylglucose under various conditions has been studied, with results contrary to the conclusions of Irvine and McGlynn. 2,3,6-Trimethyl-γ-gluconolactone is a crystalline substance the properties of which diverge widely from those ascribed to this lactone by the above authors. It is shown that dimethylmethylglucoside is readily extracted from aqueous solution by chloroform. The bearing of these results on the critical views of Irvine concerning the chemistry of sucrose and other disaccharides is discussed.

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The Preparation of Some Higher Aliphatic Sulfonic Acids

BY C. R. NOLLER AND J. J. GORDON

The work of Reychler[1a] and of McBain and his associates[1b] has shown that cetyl sulfonic acid has unique properties for the investigation of soap solutions, but it has the disadvantage that it is not very soluble in water at temperatures below 50°. Sulfonic acids giving colloidal aqueous solutions but having a lower molecular weight should be more satisfactory but none appear to have been described between C_8 and C_{16}. Accordingly the straight chain aliphatic sulfonic acids containing from nine to fourteen carbon atoms have been prepared in quantity and in a pure state and we wish to report on their preparation at the present time. The work on the physical properties of their solutions will be reported by others at a future date.

The general methods available for preparing aliphatic sulfonic acids in quantity are few in number and in general unsatisfactory. Attempts to prepare esters of sulfonic acids from ethyl chlorosulfonate and alkylmagnesium halides by Mr. Poe Liang in this Laboratory were not successful, nor did the direct oxidation of the disulfides lead to satisfactory results. The method used in the present work has been the nitric acid oxidation of the lead mercaptide, a procedure first described by Williams.[2] In all cases the starting material was the corresponding alcohol.

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(1) (a) Reychler, *Bull. soc. chim. Belg.*, *27*, 110, 217, 300 (1913); (b) Norris, *J. Chem. Soc.*, **121**, 2161 (1922); McBain and Williams, Colloid *Symposium* Annual, **7**, 105 (1929).

(2) Williams, Ph.D. Thesis, Stanford University, 1929. See forthcoming article by McBain and Williams, THIS JOURNAL (1933).

Alcohols.—Nonyl alcohol was prepared by the action of ethylene oxide on heptylmagnesium bromide; decyl, lauryl, and undecylenyl alcohols by the reduction of the methyl esters of the corresponding acids[3] by means of sodium and absolute alcohol;[4] undecyl alcohol by the catalytic reduction of undecylenyl alcohol; tridecyl alcohol by the action of formaldehyde on laurylmagnesium bromide. The alcohols all boiled over less than 3° ranges.

Bromides.—The alcohols were converted into the bromides by the method of Kamm and Marvel6 in 65 to 80% yields and boiled over a 3° range or less. It appears that two of the bromides have not been previously described. Their physical properties and analyses were as follows: myristyl bromide, b. p 175–178° at 20 mm.; & 0.9322; n_D^{20} 1.4582; Br found, 28.5, calcd 28.8. Tridecyl bromide, b. p. 164–167° at 23 mm.; d_{20}^{20} 0.9644; n_D^{20} 1.4574; Br found, 29.9, calcd. 30.4.

Mercaptans.—The method used for the preparation of the mercaptans was an adaptation of a procedure for heptyl mercaptan which had been kindly supplied to us by Mr. W. W. Hartman of the Eastman Kodak Company. The general method of preparing mercaptans by the reduction of disulfides with zinc in acid solution was first reported by Friedländer.[6]

In a 3-liter flask was placed 187 g. of sodium sulfide ($Na_2S \cdot 9H_2O$), 700 cc. of water and 32 g. of powdered sulfur and the mixture shaken, with warming on a steam-bath, until a clear solution was obtained. This was diluted with 850 cc. of methyl alcohol, and the flask fitted with a mechanical stirrer, reflux condenser and 500-cc. dropping funnel. The solution was heated to boiling and 1 mole of the alkyl bromide run in rapidly. The reaction does not begin at once but lags from one to four minutes. Heating was stopped during the addition and cautiously resumed a few minutes later. Refluxing and stirring was continued for one hour, after which time the mixture was poured into a beaker containing two or three times its volume of cold water.

After standing overnight the crude dialkyl disulfide was separated and placed with 335 cc. of approximately 50% (1 vol. concn.—2 vol. water) sulfuric acid solution in a 2-liter round-bottomed flask, fitted with a mechanical stirrer and reflux condenser. The mixture was heated to boiling, and 87 g. of zinc dust added in small portions, with the temperature near the boiling point. Then 50 cc. of concentrated sulfuric acid was added in small portions through the condenser, and gentle heating continued for ten minutes. If the heating was continued for a longer period, the reaction became very violent and foamed over. Stirring was continued for one hour, the mixture diluted with an equal volume of cold water and filtered with suction. The mercaptan layer was separated from the filtrate and the zinc residue extracted with two 200-cc. portions of methyl alcohol. The alcohol was distilled, the main portion of mercaptan added to the extracted portion and the whole washed with 150 cc. of hot water, separated and distilled at reduced pressure, from a modified Claisen flask having a 40-cm. fractionating side arm.

The sulfur content is low, indicating the probable presence of the corresponding alcohol since the latter might arise by hydrolysis of the bromide and would be difficult

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(3) Methyl caprate was obtained by the fractionation of the mixed methyl esters from the seed fat of the California bay tree, which unpublished work at this Laboratory has shown to consist of approximately one-third methyl caprate and two-thirds methyl laurate.

(4) One change in the procedure of Ford and Marvel, "Organic Syntheses," 1930, Vol. X, p. 62, for the reduction of esters was made which largely eliminated the formation of emulsions during washing, and foaming during distillation. The crude product was washed once or twice with hot water, which can be done without the formation of emulsions, the water layer separated and the oil placed in a large open beaker. If an emulsion formed during the washing, it was broken by the addition of salt. The oil was then heated in the beaker with stirring to 150–175° until foaming stopped and then transferred while hot to a distilling flask and the distillation carried out without difficulty.

(5) Kamm and Marvel, "Organic Syntheses," Vol. I, 1932, p. 23.

(6) Friedländer, Bet.,39, 1066 (1906).

TABLE I

MERCAPTANS

	Yield, %	Boiling point, °C.	Pressure, mm.	d^{20}_{20}	n^{20}_{D}	% S	
						Calcd.	Found
Nonyl[a]	80.0	100–104	20	0.8386	1.45197	20.0	19.7
Decyl[b]	81.5	125–127	19	.8410	1.45367	18.4	18.0
Undecyl	76.0	138–141	21	.8432	1.45816	17.0	16.7
Lauryl	81.0	153–155	24	.8450	1.45886	15.8	15.1
Tridecyl	87.5	162–166	22	.8468	1.45906	14.8	14.0
Myristyl	83.5	176–180	22	.8484	1.46005	13.9	12.9

[a] Ellis and Reid, THIS JOURNAL, 54,1684 (1932). [b] V. Braun, Teuffert and Weissbach, *Ann.*, 472, 139 (1929).

to remove by distillation.[7] The mercaptans were free of halogen and sufficiently pure for our purpose since the impurities were removed in the subsequent purification of the lead mercaptide and sulfonate.

Lead Mercaptides and Sulfonates.—A solution of 0.8 mole of the mercaptan in 750 cc. of 95% alcohol was added slowly, with rapid stirring, to a solution of 150 g. of lead acetate in 750 cc. of 50% alcohol. In preparing the solutions of the higher mercaptans, lauryl, tridecyl and myristyl, it was necessary to add a small amount of ether to get the mercaptan entirely into solution. The mercaptide precipitated as a bright orange salt which immediately turned to a light canary yellow color. This was filtered with suction and washed twice with water and once with one liter of acetone and dried. The dry salt was powdered and added, in small portions, to one liter of 50% nitric acid in a 5-liter round-bottomed flask. The mixture was kept well mixed by shaking the flask after adding each portion of salt. It was necessary in some cases to heat the acid slightly after adding the first two or three portions to start the reaction and to prevent a too vigorous reaction due to an accumulation of unreacted mercaptide. A white salt settling to the bottom of the flask and the evolution of copious brown fumes indicate the progress of the reaction. After all the mercaptide had been added the mixture was allowed to stand for one hour with occasional shaking, diluted with 3 liters of cold water and filtered with suction. The salt was washed twice with water, filtered as dry as possible and then extracted with two or more 1500-cc. portions of hot acetone, until no further precipitate could be obtained upon chilling the filtrate in a freezing solution.

TABLE II

LEAD SULFONATES

Mercaptan used	Yield, %	Pb, %	
		Calcd.	Found[b]
Nonyl	16.7[a]	33.3	33.0
Decyl	75.5	31.9	31.5
Undecyl	83.0	30.5	30.4
Lauryl	76.0	29.3	29.4
Tridecyl	58.8	28.2	28.3
Myristyl	68.5	27.2	27.5

[a] The low yield of lead nonylsulfonate appears to be due to its greater solubility in dilute nitric acid. [b] Analyses for lead were by titration with ammonium molybdate solution according to Treadwell-Hall, "Analytical Chemistry," 6th ed., Vol. II, p. 618.

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(7) The method for the analysis of mercaptans of Kimball, Kramer and Reid [THIS JOURNAL, 43, 1199 (1921)] did not give a satisfactory end-point, probably because the disulfides formed are for the most part insoluble solids which enclose unreacted mercaptan. Since this work was completed Sampey and Reid [*ibid.*, 64, 3404 (1932)] have applied the iodimetric method to benzene solutions but we have not tried this modification for the higher mercaptans

On cooling the acetone extracts of the lead sulfonates, a white crystalline product usually separated, which in the case of the lead lauryl sulfonate melted at 45–46°. No attempt was made to identify these impurities.

Sulfonic Acids.—A 6-mm. glass tube drawn out to 1.5 mm. at one end was sealed into the wall of a 500-cc. round-bottomed flask in such a way that the narrow end extended to the bottom of the flask. The flask was connected to a reflux condenser by means of a ground-glass joint. Fifty grams of lead salt and 250 cc. of dry isopropyl alcohol were placed in this flask and well mixed. The suspension was heated to refluxing for twenty to thirty minutes while dry hydrogen chloride was introduced through the small tube. The progress of the reaction was easily followed by the appearance of the salt. The lead sulfonate remained in suspension in the alcohol and was of a lustrous white appearance, whereas the lead chloride was a flat white and settled to the bottom of the flask, leaving a clear solution above it. After complete decomposition the suspension was cooled and the lead chloride filtered onto a sintered glass filter.

The filtrate was transferred to a 750-cc. flask fitted to a distilling bend 22 mm. in diameter with a ground glass connection. The solvent was evaporated at 3-4 mm. pressure keeping an external bath at 80–90°. It was not possible to remove all of the solvent in this way, but the solutions were evaporated until they became very viscous, or, in some cases, began to crystallize Then 150 cc. of freshly distilled ether was added and the whole was transferred to a 500-cc. separatory funnel. One hundred and fifty cubic centimeters of water was added and the mixture thoroughly shaken. The ether layer was removed and the water solution was extracted with three 100-cc. portions of ether. The aqueous solution was then drawn from the funnel into an open beaker and evaporated at reduced pressure over calcium chloride. It was necessary to control carefully the pressure, to keep the solution from foaming over the beaker. As the solution became more concentrated it gradually became more viscous until it finally set to a pasty mass of liquid crystal form. It was impossible to dry it further over calcium chloride, so it was transferred to another desiccator over phosphorus pentoxide and the drying was continued at the same pressure. It was necessary to break up lumps of solid matter occasionally during this further drying. The final product was a white crystalline solid, analysis by titration showing it to be a monohydrate of the sulfonic acid. Anhydrous samples for analysis were dried at 3 mm. and 80°.

TABLE III

SULFONIC ACIDS

Lead sulfonate used	Yield, %	Melting point, °C. Hydrate	Anhyd.[b]	Neutral equivalent Hyd. Found	Anhyd. Calcd.	Found	S, % Calcd.	Found
Nonyl[a]	84.7	...	46	...	208.2	210.0	15.38	15.30
Decyl[a]	60.0	...	46.5	...	222.2	223.5	14.40	15.00
Undecyl	84.0	40–41	49	253.0	236.2	235.9	13.55	13.46
Lauryl	92.0	43–45	52	267.5	250 2	249.5	12.79	12.82
Tridecyl	80.2	48–49	58	281.3	264.2	266.4	12.11	12.01
Myristyl	81.0	55–56	65.5	295.5	278.2	277.0	11.50	11.42

[a] Nonyl and decyl sulfonic acids were obtained directly in the anhydrous state. [b] The melting points for the anhydrous products are not capillary melting points but are approximate values taken in the tubes in which the sample was dehydrated

The benzylaniline salts of the sulfonic acids were found to be non-hygroscopic, were readily purified by crystallization from ether containing a small amount of alcohol, and possessed sharp melting points.[8] While the melting points do not vary as much as

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(8) Unpublished work with M. L. Farrow has shown that benzylaniline salts are satisfactory derivatives for sulfonic acids in general.

might be desired, the compounds are readily distinguished by titrating their hot solutions with standard alkali.

TABLE IV

BENZYLANILINE ALKYLSULFONATES

	Melting point, °C.	N, % Calcd.	N, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
Nonyl	90.5–91.0	3.58	3.70	391	396
Decyl	84.0–84.5	3.45	3.49	405	406
Undecyl	84.6–84.7	3.28	3.34	419	421
Lauryl	91.0–91.2	3.23	3.18	433	435
Tridecyl	87.5–88	3.13	3.09	447	445
Myristyl	82.5–82.7	3.04	2.95	461	462

Summary

The normal aliphatic mercaptans and sulfonic acids containing from nine to fourteen carbon atoms have been prepared in quantity and in a pure state. The benzylaniline salts of the sulfonic acids are described as derivatives.

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Acetylene Polymers and their Derivatives. VI. Vinylethinylmagnesium Bromide and Some of its Reactions

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

As might be expected from its structure, vinylacetylene (I) reacts rapidly with ethylmagnesium bromide. The reaction proceeds smoothly and apparently involves only the acetylenic hydrogen; the behavior of the product indicates that it is vinylethinylmagnesium bromide (II). It reacts in the typical manner with a variety of reagents.

Acetone yields vinylethinyldimethylcarbinol (III), a colorless liquid whose structure is established by its hydrogenation to *n*-butyldimethylcarbinol. On standing, it polymerizes to a colorless, transparent resin.

The action of carbon dioxide on vinylethinylmagnesium bromide apparently gives vinylpropiolic acid (IV), but it was not found possible to isolate this substance in a state of high purity. Above 110° it polymerizes explosively, and even at lower temperatures it is rapidly converted into a tough, insoluble, rather elastic mass.

The products (V and VI) obtained from α-naphthyl isocyanate and from triphenylchloromethane are stable crystalline solids.

$$\begin{array}{ccc} CH_2{=}CH{-}C{\equiv}CH & CH_2{=}CH{-}C{\equiv}C{-}MgBr & CH_2{=}CH{-}C{\equiv}C{-}COH(CH_3)_2 \\ \text{I} & \text{II} & \text{III} \end{array}$$

$CH_2{=}CH{-}C{\equiv}C{-}COOH$ IV

$CH_2{=}CH{-}C{\equiv}C{-}CO{-}NH{-}C_{10}H_7$ V

$CH_2{=}CH{-}C{\equiv}C{-}C(C_6H_5)_3$ VI

Experimental Part

Preparation of **Vinylethinylmagnesium** Bromide (II).—The reaction vessel was provided with a refrigerated return condenser (ice–salt) and dropping funnel. The vinylacetylene (10 to 20% excess) dissolved in ether was added in portions with continuous stirring to the ethylmagnesium bromide. The reaction proceeded smoothly with sufficient evolution of hear to keep the rtlier refluxing gently. The reaction product remained dissolved in the ether.

Vinylethiildiiethylcarbinol (III).—Forty grams of purified acetone was added slowly to a 15% excess of vinylethinylmagnesium bromide. The product of the reaction distilled without residue at 50–59° (15 mm.). On redistillation, 40 g. of a colorless liquid boiling at 59–61' (17 mm.) was collected. The yield in pure vinylethinyldimethylcarbinol was 53%. B. p. 67° (24 mm.); n_D^{20} 1.4778; d_4^{20} 0.8872; M_R calcd , 33.32; found, 35.07. Exaltation, 1.75.

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09; mol. wt., 110. Found: C, 76.18; H, 8.88; mol. wt. (cryoscopicin benzene), 119.

The carbinol became increasingly viscous on standing. After two weeks it was a hard, tough, transparent mass insoluble in the common organic solvents. This transformation was accompanied by the absorption of oxygen; the analytical values for carbon and hydrogen became progressively lower. The values for the completely polymerized product were C, 70.7, and H, 8.7. The polymerization was greatly retarded by the presence of hydroquinone.

Hydrogenation of **Vinylethinyldimethylcarbinol**.—Twenty grams of the carbinol was dissolved in 75 cc. of alcohol. Four-tenths of a gram of platinum oxide was added and the mixture was shaken in a reduction apparatus. It absorbed 0.506 mole of hydrogen in forty-five minutes, or about 93% of the theoretical amount, calculated for three moles of hydrogen absorbed per mole of carbinol. After evaporation of the alcohol the residue distilled at 71–72° at 48 mm. It was a colorless liquid with a pleasant camphor-like odor. Its physical constants agreed closely with those given in the literature for dimethylbutylcarbinol.

	Found		Given in the literature[a]
B. p.	139.5–141° (761 mm.)	B. p.	141–142° (755 mm.)
n_D^{23}	1.4189	n_D	1.41592
d_{20}^{20}	0.817	d	0.8155

[a] Henry and Dewaei, Bull. *Acad. Roy.* Belg., 957 (1908); Chem. *Z.*, I, 1854 (1909).

Anal. Calcd. for $C_7H_{16}O$: C, 72.41; H, 13.79. Found: C, 72.31, 72.37; H, 13.68, 13.64.

Vinylpropiolic Acid.—One mole of vinylethinylmagnesium bromide was treated with dry carbon dioxide at 0° until a color test showed the absence of any RMgBr. The product was then decomposed with water and the aqueous solution was submitted to continuous extraction with ether for eight hours. The solvent was evaporated in *vacuo*. The residue weighed 50 g. (calcd., 96 g.). Attempts to distil the product at this stage by the usual methods always resulted in explosions. A partially successful distillation was effected at low pressure (about 0.05 mm.) in an all-glass apparatus. This consisted of a flask sealed to a receiver cooled in liquid air. The flask was heated to about 60°. Evaporation occurred at a moderately rapid rate, and the distillate froze to a crystalline solid in the receiver. It became liquid below room temperature. On redistillation in a stream of carbon dioxide most of the volatile product came over between **64** and **71**" at **2** mm. It was a colorless, water-soluble liquid which turned yellow on standing. Its molecular weight, determined by titration with $N/10$ sodium hydroxide, was **102,** instead of the calculated value **96.** The product was evidently not quite pure. It reduced permanganate instantly in acetone solution.

A tube containing a sample of the acid was evacuated with a water-pump and sealed off. The tube was heated for eighty-five minutes at 75°, at the end of which time a rubber-like yellow substance had formed. This was insoluble in water, alcohol, ether, benzene and acetic acid at the boiling points of these solvents. It was partly soluble in hot sodium hydroxide, imparting a yellow color to the solution, from which an amorphous solid separated on neutralization.

a-Naphthylamide **of Vinylpropiolic** Acid (V).—A solution of 9 g. of a-naphthyl isocyanate in anhydrous ether was added slowly to an excess of vinylethinylmagnesium bromide. The reaction proceeded smoothly. The mixture was refluxed for thirty minutes, then poured onto crushed ice. On extraction of the aqueous solution with ether, **1.5** g. of dinaphthylurea was left undissolved. On evaporation of the ether solution, a yellowish solid separated. After two crystallizations from 50% alcohol it was obtained in the form of small yellowish needles melting at **125** to 126° (copper block); yield, **9** g. It was readily soluble in ether, benzene, methanol and ethanol. It reduced permanganate in acetone solution very rapidly. In chloroform solution it absorbed bromine slowly with the evolution of hydrogen bromide.

Anal. Calcd. for $C_{15}H_{11}ON$: C, **81.44;** H, **4.97;** mol. wt., **221.** Found: C, **81.50, 81.27; H,** 4.92, 4.85; mol. wt. (in boiling ethylene chloride), **221,219.**

Vinylethinyltriphenylmethane (VI).—A slight excess of vinylethinylmagnesium bromide was treated with a solution of **10** g. of triphenylchloromethane in anhydrous ether. After completion of the reaction, the mixture was worked up as usual. The ether solution left on evaporation **7.5** g. of a yellowish crystalline solid. After recrystallization from hot alcohol, it melted at 134–135° (copper block). It reduced permanganate in acetone solution and absorbed bromine, though slowly, in chloroform solution.

Anal. Calcd. for $C_{23}H_{18}$: C, **93.87;** H, **6.12;** mol. wt., **294.** Found: C, **94.17, 93.52; H,** 6.14, 6.24; mol. wt. (in boiling benzene), **320,315.**

Summary

Vinylacetylene reacts with ethylmagnesium bromide yielding vinylethinylmagnesium bromide. This behaves in the typical manner toward acetone, carbon dioxide, a-naphthyl isocyanate and triphenylchloromethane. The derivatives thus produced are described.

WILMINGTON, DELAWARE

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Acetylene Polymers and their Derivatives. VII. Sodium Vinylacetylide and Vinylethinylcarbinols

BY WALLACE H. CAROTHERS AND RALPH A. JACOBSON

Vinylacetylene, like other true acetylenic compounds, reacts with Grignard reagents to form the corresponding organo magnesium halide, and this may be used to introduce the vinylethinyl group into compounds of various types.[1] The present paper is concerned with the formation of sodium vinylacetylide and with its use in a similar manner, especially in the synthesis of vinylethinylcarbinols.

Sodium vinylacetylide is readily obtained by the action of vinylacetylene on metallic sodium. The metal may be applied directly to the liquid hydrocarbon, or the latter may be diluted with an inert solvent such as ether, toluene or liquid ammonia. The reaction occurs with great rapidity if the sodium is dissolved in liquid ammonia. These methods, however, have the disadvantage that the acetylide produced is frequently contaminated with appreciable amounts of polymeric material. More uniformly satisfactory results are obtained by the action of powdered sodamide on the hydrocarbon. The latter is preferably dissolved in ether or liquid ammonia.

The sodium vinylacetylide obtained in this manner is a dusty, white powder, and vinylacetylene is regenerated in high yield when it is cautiously treated with water in the presence of a diluent. Its stability is sufficient to permit its storage for two or three days in a stoppered bottle, and with some care it can be handled in the presence of air. However, if the air is moist the acetylide sometimes ignites spontaneously. It attacks many organic reagents with explosive violence, but cooling and dilution permit sufficient control to obtain smooth reaction in most cases. Isolation of the sodium compound is not necessary for its application as a reagent; the intended reactant is preferably added directly to the mixture resulting from the action of sodamide on vinylacetylene.

In dealing with aldehydes and ketones a still simpler and more satisfactory procedure consists in adding powdered sodamide in portions to a mixture of the carbonyl compound with vinylacetylene. In most cases it is advantageous to have present a diluent such as ether. With simple aliphatic and alicyclic ketones this method is very satisfactory. The yields are good and large scale operations are much simpler than with the vinylethinylmagnesium halides. However, sodium vinylacetylide has a more limited range of applicability in the synthesis of carbinols than has vinylethinylmagnesium bromide. Aliphatic aldehydes are partly resinified by the sodium compound, and unsaturated aldehydes and ketones are

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(1) Carothers and Berchet, THIS JOURNAL, 66, 1094 (1933)

usually resinified completely. The magnesium compound, however, even with very sensitive aldehydes and ketones, generally yields the expected monomeric carbinols.[2]

Vinylethinyldimethylcarbinol has already been described[1] and the other carbinols listed in Table II resemble it in their properties. They react readily with bromine and decolorize permanganate; in the presence of platinum they are smoothly hydrogenated to the corresponding n-butylcarbinols. They can be distilled in *vacuo* without decomposition, but if the temperature of distillation is too high the tertiary carbinols tend to lose water with the production of the corresponding substituted divinylacetylenes. Vinylethinyldi-n-propylcarbinol, for example, thus leads to the compound $C_2H_5—CH=C(C_3H_7)—C\equiv C—CH=CH_2$. Divinylacetylene itself was obtained by heating vinylethinylmethylcarbinol with *p*-toluenesulfonic acid.

The tertiary carbinols all polymerize spontaneously on standing.[3] The transformation sets in rather quickly and progresses to the stage of a thick sirup during the course of a few days. The mixture then sets to a tough rather elastic mass, but the final product, a hard, transparent glass-like mass, is obtained only after several weeks or months. The transformation is greatly accelerated by certain catalysts, e. g., benzoyl peroxide, especially in the presence of light. The final glass-like products adhere very tenaciously to glass. They are insoluble in the common organic solvents. The polymerization of the carbinols also proceeds more rapidly at elevated temperature, e. g., 100°, but the final product obtained under these conditions is fusible and completely soluble in the common organic solvents. The spontaneous polymerization of the carbinols is strongly inhibited by the presence of a small amount of hydroquinone. The secondary carbinols polymerize very much more slowly than the tertiary carbinols.

Experimental Part

Preparation of **Sodium Vinylacetylide.**—Powdered sodamide (19.5 g., 0.5 mole) was slowly added to a solution of 75 g. of vinylacetylene in 250 cc. of liquid ammonia. The mixture was stirred for six hours and the ammonia evaporated in a stream of nitrogen, finally at 60°. The residue was a white powder (38 g., calcd. 37 g.) which showed a tendency to ignite spontaneously when exposed to the air. It was covered with toluene, and water was slowly added with constant stirring at 75°. The acetylide finally dissolved without appreciable residue in the aqueous layer. Vinylacetylene was distilled from the mixture and collected in a cold receiver. The yield was 21.3 g. or 82%.

Preparation of **the Carbinols.**—The general procedure used for the preparation of the tertiary carbinols is illustrated by the following example. The reaction mixture consisted of 555 g. (7.7 moles) of methyl ethyl ketone (Eastman Kodak pract.), 551 g. (10.6 moles) of vinylacetylene, and 500 cc. of dry ether. The solution was contained in

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(2) Unpublished results.

(3) The behavior of the vinylethinylcyclopentanol was exceptional. It had not polymerized after standing for one year at the ordinary conditions.

a 3-necked flask provided with a mercury-sealed stirrer and a coil condenser, which in turn was connected to a trap. The reaction flask and trap were surrounded with carbon dioxide snow and the coil condenser was kept cold in the same manner. To the cold solution was slowly added 300 g. (7.7 moles) of powdered sodamide and stirring was continued for a total of six hours. The reaction mixture was made acid to litmus by means of 10% sulfuric acid, the ether layer separated and dried with sodium sulfate, and then distilled in a vacuum; 677 g. of pure vinylethinylmethylethylcarbinol was obtained; yield 71%. The carbinol was stabilized with 0.1% hydroquinone in order to prevent spontaneous polymerization.

The same procedure was applied to the preparation of the secondary carbinols but the results were less satisfactory. The preparation of vinylethinylmethylcarbinol is used as an illustration. To a solution of 44 g. (1 mole) of freshly distilled acetaldehyde and 75 g. of vinylacetylene in 75 cc. of dry ether at −10° was slowly added 39 g. of powdered sodamide. After a few grams of sodamide had been added, the mixture became so gummy that additional ether was added. Finally, the mixture formed a cake and stirring was discontinued. After four hours the cake was broken up with a stirring rod, more ether added, and the suspension stirred at room temperature for three hours. The reaction mixture was allowed to stand overnight and then decomposed with water and dilute sulfuric acid. The mixture was extracted several times with ether, and the latter dried with sodium sulfate and distilled. A considerable quantity of ether-insoluble resin remained in the reaction mixture. After removal of the ether and a small amount of low boiling liquid, 25 g. (26%) of vinylethinylmethylcarbinol was collected. It was a colorless liquid with an alcoholic odor slightly resembling that of butyl alcohol. It reacted with dinitrobenzoyl chloride to form the **3,5-dinitrobenzoate of vinylethinylmethylcarbinol**, white needles from dilute alcohol; m. p. 106–106.2°.

Anal. Calcd. for $C_{13}H_{10}N_2O_6$: C, 54.27; H, 3.41. Found: C, 54.34; H, 3.47.

Catalytic Reduction of the **Vinylethinylcarbinols.**—The carbinols derived from acetone and from methyl ethyl ketone absorbed four atoms of hydrogen very rapidly when dissolved in alcohol and shaken with hydrogen in the presence of Adams' platinum oxide catalyst. The resulting *n*-butylcarbinols corresponded in their properties with those already reported in the literature, and the yields were almost quantitative. Hydrogenation of the carbinols derived from methyl octyl ketone and from acetophenone yielded the new saturated carbinols described below.

***n*-Butylmethyloctylcarbinol.**—Colorless liquid, b. p. (3 mm.) 94°; n^{20}_{D} 1.4418; d^{20}_{4} 0.8318; M_R calcd., 68.38; M_R found, 68.03.

Anal. Calcd. for $C_{14}H_{20}O$: C, 78.50; H, 14.02. Found: C, 77.20, 77.30; H, 14.18, 14.25.

***n*-Butylmethylphenylcarbinol.**—Colorless liquid, b. p. (6 mm.) 107 to 109°; n^{20}_{D} 1.5118; d^{20}_{4} 0.9616; M_R calcd., 55.52; M_R found, 55.52.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 81.02, 81.16; H, 10.38, 10.24.

***n*-Propyl-5-octadiene-1,5-ine-3.**—When the attempt was made to distil vinylethinyldi-n-propylcarbinol in *vacua* in a flask provided with a long column, dehydration occurred and the non-aqueous distillate was the hydrocarbon *n*-propyl-5-octadiene-1,5-ine-3. On redistillation it was obtained as a pale yellow liquid having a characteristic odor; b. p. (6 mm.) 57 to 58°; d^{20}_{4} 0.8047; n^{20}_{D}, 1.4949; M_R calcd., 50.06; M_R found, 53.62. The sample was perhaps not quite pure.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 87.47, 90.27, 87.73; H, 11.11, 9.94, 10.61.

Preparation **of Divinylacetylene** by the Dehydration of **Vinylethinylmethylcarbinol.**—To 25 g. of *p*-toluenesulfonic acid in a 500-cc. flask provided with a stirrer, separa-

TABLE I

ANALYTICAL DATA FOR VINYLETHINYLCARBINOLS

Structural formula of carbinol	Empirical formula	Calcd. C	Calcd. H	Calcd. Mol. wt.	Found C	Found H	Found Mol. wt. in freezing benzene
$CH_3CHOH—C\equiv C—CH=CH_2$	C_6H_8O	75.00	8.33	96	74.66	8.34	104
n-$C_3H_7CHOH—C\equiv C—CH=CH_2$	$C_8H_{12}O$	77.42	9.67	124	76.83	9.83	127
$(CH_3)_2C(OH)—C\equiv C—CH=CH_2$	$C_7H_{10}O$	76.36	9.09	110	76.18	8.88	119
$CH_3(C_2H_5)C(OH)—C\equiv C—CH=CH_2$	$C_8H_{12}O$	77.42	9.67		77.09	9.87	
$(C_2H_5)_2C(OH)—C\equiv C—CH=CH_2$	$C_9H_{14}O$	78.26	10.14	138	78.61	10.09	136, 141
$(n$-$C_3H_7)_2C(OH)—C\equiv C—CH=CH_2$	$C_{11}H_{18}O$	79.52	10.84	166	79.89	11.14	167, 171
$CH_3(C_8H_{17})C(OH)—C\equiv C—CH=CH_2$	$C_{14}H_{24}O$	80.77	11.54		80.17	10.87	
$(CH_2)_4C(OH)—C\equiv C—CH=CH_2$	$C_9H_{12}O$	79.41	8.82	136	79.36	8.99	145, 145
$(CH_2)_5C(OH)—C\equiv C—CH=CH_2$	$C_{10}H_{14}O$	80.00	9.33	150	79.70	9.29	137, 144[a]
$CH_3(C_6H_5)C(OH)—C\equiv C—CH=CH_2$	$C_{12}H_{12}O$	83.72	6.97	172	83.23	7.08	173

[a] In boiling benzene.

TABLE II

PHYSICAL PROPERTIES OF VINYLETHINYLCARBINOLS

Ketone or aldehyde reactant	Formula of carbinol produced	B. p., °C.	Mm.	d_4^{20}	n_D^{20}	M_R calcd.	M_R found	Exaltation
Acetaldehyde	$CH_3—CHOH—C\equiv C—CH=CH_2$	65	22	0.9112	1.4851	28.97	30.20	1.23
Butyraldehyde	n-$C_3H_7—CHOH—C\equiv C—CH=CH_2$	74–76	10	.8919	1.4775	38.21	39.32	1.11
Acetone	$(CH_3)_2C(OH)—C\equiv C—CH=CH_2$	68	24	.8872	1.4778	33.32	35.08	1.76
Methyl ethyl ketone	$CH_3(C_2H_5)C(OH)—C\equiv C—CH=CH_2$	75	20	.8878	1.4802	38.21	39.90	1.69
Diethyl ketone	$(C_2H_5)_2C(OH)—C\equiv C—CH=CH_2$	62	4	.8875	1.4800	42.82	44.17	1.35
Dipropyl ketone	$(n$-$C_3H_7)_2C(OH)—C\equiv C—CH=CH_2$	98–99	22	.8738	1.4745	52.05	53.44	1.39
Methyl octyl ketone	$CH_3(C_8H_{17})C(OH)—C\equiv C—CH=CH_2$	98–100	5	.8681	1.4734	65.91	67.26	1.35
Cyclopentanone	$(CH_2)_4C(OH)—C\equiv C—CH=CH_2$	104–105	7	1.0181	1.5228	40.62	(40.79)	(0.17)
Cyclohexanone	$(CH_2)_5C(OH)—C\equiv C—CH=CH_2$	84–85	2	0.9742	1.5169	45.24	46.57	1.33
Acetophenone	$CH_3(C_6H_5)C(OH)—C\equiv C—CH=CH_2$	125–126	4	m. p. 40–41 °				

tory funnel, and condenser was slowly added 20.8 g. of vinylethinylmethylcarbinol. The flask was warmed on a water-bath to start the reaction, after which it proceeded vigorously. After two hours, the condenser was replaced by a distilling column and the contents of the flask distilled in *vacuo*. Divinylacetylene distilled from the mixture and collected in a trap surrounded by solid carbon dioxide and acetone. The divinylacetylene was not further purified, but was converted into the hexabromide. The melting point of this hexabromide was identical with that of the hexabromide from a known sample of divinylacetylene. The melting points were as follows

Hexabromide from above synthesis	m. p. 105–106°
Hexabromide from known sample of divinylacetylene	104106°
Mixed m. p.	105–106°

Polymerization of the Carbinols.—The behavior of vinylethinylmethylethylcarbinol is typical of the tertiary carbinols. On standing in a stoppered bottle its viscosity increased very rapidly during the first few days, and at the end of a week the product was a thick, colorless, transparent sirup. After three weeks it had set to a tough, elastic, rather rubber-like mass which still contained a considerable proportion of unchanged carbinol. After six weeks it had changed to a very hard, translucent mass.

Fifty grams of vinylethinylmethylethylcarbinol containing 0.5 g. of benzoyl peroxide was exposed to a Cooper–Hewitt light (mercury arc in glass). The product obtained after seventy-two hours was a hard, transparent, pale yellow, glass-like resin. It was insoluble in the common organic solvents. When heated it softened somewhat at 125 to 150°, but it did not liquefy completely even at much higher temperatures.

Twenty-five grams of the carbinol containing 0.25 g. of benzoyl peroxide was exposed to a 150-watt Mazda light. In four days a product similar to that described in the preceding example was obtained.

Twenty-five grams of the carbinol containing 0.25 g. of uranyl nitrate was exposed to a Cooper–Hewitt light. In seventy-two hours, a hard, transparent, amber-colored resin was obtained. When no catalyst was present under the same conditions, the transformation to a hard resin required about one week.

A sample of vinylethinylmethylethylcarbinol was heated for several hours at 100° while a slow stream of air was bubbled through it. The product was a brown sirup. At room temperature it solidified to a brittle resin which dissolved readily in the common organic solvents.

Summary

Sodium vinylacetylide obtained by the action of sodium or of sodamide on vinylacetylene is a very reactive white powder which shows a tendency to ignite spontaneously in the air. Under properly controlled conditions it is a convenient reagent for introducing the vinylethinyl group into reactive organic compounds. Vinylethinylcarbinols are readily obtained by treating a mixture of vinylacetylene and a ketone with sodamide. The same method can also be applied to aldehydes but with less favorable results. Nine new carbinols prepared by this method are described.

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Co-Ferments and Banana Respiration

BY J. M. NELSON AND CATHARINE HEMPERLY

The metabolism of respiration in the case of the higher plants plays a dominating role in the ripening and storage of fruit, the curing of hay, tobacco, grains, etc. Although considerable work has been and is being done on the chemistry of respiration as it is related to fermentation by yeast and to the glycolysis in muscle tissue, our knowledge along these lines concerning plant respiration is still relatively meager. The present paper is an account of the study of glycolytic activators present in the pulp and juice of bananas.

The presence of zymasic activators in plant material, such as pea meal, has been shown by Bodnar and Hoffner.[1] Euler and Steffenburg[2] added boiled apple juice as well as a boiled aqueous extract of the fruit to some yeast apo-zymase preparation, but observed practically no stimulation of zymasic activity. From other results, however, they concluded that these experiments did not necessarily show the absence of cozymasic activators, but rather the presence of inhibitors, probably phenolic in character, which tend to mask the presence of the activators in the extracts from apples.

The present authors, in connection with some work on the chemical changes involved in the ripening of bananas, find the juice from this fruit to contain co-ferments. The presence of these co-ferments or activators in bananas was established by much the same procedure as that used in the case of yeast and muscle tissues. Boiled aqueous extracts of the fruit were added to a mixture of yeast apo-zymase, glucose, sodium phosphate, hexose diphosphate and water, contained in the reaction flask of a Warburg–Barcroft respiration apparatus and the rate and amount of carbon dioxide given off measured.

Apo-zymase Preparations.—These were obtained by stirring several grams of air or acetone dried brewer's yeast with twenty times its weight of water for fifteen minutes, centrifuging, and repeating the washing. For some lots of yeasts, four washings were necessary in order to remove most of the cozymase. Preparations obtained in this way produced very little fermentation when mixed with solutions containing glucose, sodium phosphate and hexose diphosphate. Dried pea meal was also used without washing in some instances as the apo-zymase preparation since very little fermentation occurs when the meal is added to a solution of glucose, disodium phosphate and hexose diphosphate. The yeast apo-zymase preparations were more active than the pea meal and therefore mostly used in this work.

Method for Determining Accelerating Effect of the Co-ferment.—The Warburg–Baraoft apparatus[3] was used; described briefly, it consisted of a 50-cc. flask, containing the reaction mixture of co-ferment, ferment and substrate, attached to a manome-

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(1) Bodnar and Hoffner, *Biochem. Z.*, 165, 145 (1925).

(2) Euler and Steffenburg, Z. *physiol. Chem.*, 175, 38 (1928).

(3) Warburg, *Biochem. Z.*, **142**, 317 (1923): **152**, 51 (1924); 214, 5 (1929).

ter for measuring the carbon dioxide evolved. The reaction flask was immersed in a constant temperature bath, kept at 35° and shaken continuously by a mechanical device attached to a motor.

Co-ferment Preparations from Bananas.—The most convenient and effective preparations of co-ferment were made by grinding in a mortar, fresh yellow ripe bananas with half their weight of water, centrifuging and boiling the supernatant liquid for two to three minutes. Green bananas can also be used for preparing the co-ferment extract, or banana juice obtained by mixing banana pulp with sand and infusorial earth and pressing the mixture in a hydraulic press using about **2000** pounds pressure. Some extracts were also prepared using commercial banana flour.

Activity of Co-ferment **Preparations.—Apo-zymase** preparation made from 4 *g.* of dried brewer's yeast. To this was added 10 cc. of 30% glucose solution, **4** cc. of 0.66 M sodium phosphate solution (PH 6.9), and **3** cc. of a 4% hexose diphosphate solution. The mixture (*PH* **6.4)** was then diluted to **40** cc. and **2** cc. of the resulting suspension was pipetted into respiration flasks containing the following material: **(1)** one cc. of distilled water; **(2)** one **cc**. of ripe banana extract (prepared as described above); **(3)** one cc. of green banana extract; (4) one cc. of extract from zymin (acetone dried yeast extracted as described above); *(5)* one cc. of extract from ripe bananas **(20** *g* of ripe banana pulp ground in a mortar with **100 cc**. of acetone, and repeated twice more when a fine powder **was** obtained. This powder was extracted with ten times its weight of water); (6) half a cc. of extract *as* in **2** and **0.5** cc. of extract as in 3.

Time in minutes	Cc of carbon dioxide given off 1	2	3	4	5	6
30	. . .	**0.34**	**0.06**	**1.78**	**0.28**	**0.21**
60	. . .	.57	.14	**3.41**	.58	**.38**
90	Trace	.71	**.19**	**4.29**	**.81**	.47

The values for the ripe banana extracts, columns **2** and **5,** are larger than those for the extract from green bananas, column **3,** indicating the presence of more co-ferment in the ripe than in the green fruit. The values in column *6* correspond to about the mean for the values in columns **2** and **3,** indicating that there was no inhibitor present in the green banana extract causing the low values in column **3.**

The accelerating influence of the co-ferment from banana on yeast apo-zymase action is considerably less than that of the yeast cozymase as can be seen by comparing columns **2** and **5.**

Stability of **the** Banana Co-ferment.—A water extract of ripe banana was prepared by grinding the pulp with an equal weight of water, centrifuging and boiling the supernatant liquid for two to three minutes. This extract had *PH* **5.0.** The extract was subjected to the following conditions. **(A)** To a portion of the extract sufficient hydrochloric acid was added to make the solution about **0.1** M in HCl and *PH* about 1. This acid solution was allowed to stand at room temperature for an hour and then neutralized with a solution of sodium hydroxide until the Pa was 5.2. **(B) A** sodium hydroxide solution was added to another portion of the extract until the *PH* of the solution was **9.4** This was allowed to stand at room temperature for an hour and then neutralized with hydrochloric acid until the PH became **4.8.** (C) **A** third portion of the above banana extract was evaporated to a sirupy mass on the water-bath (one hour duration of heating) and then diluted with water to the original volume. (D) A fourth portion of the banana extract was brought to *PH* 6.4 with dilute sodium hydroxide, then heated on the water-bath as in C for one hour, and finally diluted to the original volume. Five cc. portions of a mixture, consisting of yeast apo-zymase, glucose, sodium phosphate and hexose diphosphate, similar to apo-zymase mixture in previous experiments, were pipetted into respiration flasks containing the following: (1) two cc. of water;

(2) two cc. of solution A; (3) two cc. of solution B; (4) two cc. of solution C; (5) two cc. of solution D, and (6) two cc. of original extract.

Time in minutes	Cc. of carbon dioxide evolved 1	2	3	4	5	6
60	0.00	0.51	0.09	0.28	0.18	0.64
120	.00	.85	.14	.55	.34	1.12

The above figures show that the co-ferment in the banana extract is greatly inactivated by alkali (solution B and column 3) and by heating at P_H 6.4 (solution D and column 5). On the other hand the co-ferment is more resistant toward acid and in both of these behaviors the banana co-ferment resembles yeast cozymase.[4]

Relation between Amount of Co-ferment and Amount of Carbon Dioxide Evolved.—Some ripe banana extract, prepared as in the previous set of experiments, was brought to P_H 6.2 and then 1 cc. of 0.66 *M* sodium phosphate added, giving a solution of P_H 6.4. Five cc. of a yeast apo-zymase mixture, similar to that used in the previous set of experiments, was pipetted into each of a series of respiration flasks which contained, respectively: (1) six cc. of water (the water used in this set of experiments contained the same amount of added sodium phosphate as the banana extracts); (2) one cc. of banana extract and 5 cc. of water; (3) two cc. of extract and 4 cc. of water; (4) four cc. of extract and 2 cc. of water; (5) five cc. of extract and 1 cc. of water; (6) six cc. of extract.

Time in minutes	Cc. carbon dioxide evolved 1	2	3	4	5	6
30	0.03	0.03	0.06	0.25	0.38	0.51
60	.05	.07	.13	.43	.64	.84
120	.08	.13	.22	.63	.91	1.20

These values show that there is a gradual increase in the volume of carbon dioxide given off as the amount of added extract is increased.

Influence of Magnesium Chloride and Acetic Aldehyde.—Five cc. of yeast apo-xymase mixture, prepared as in previous experiments, was added to respiration flasks containing the following material: (1) two and 0.6 cc. of water; (2) two cc. of ripe banana extract (prepared as in previous set of experiments) and 0.6 cc. of a 2% aqueous solution of acetic aldehyde; (3) two cc. of ripe banana extract and 0.6 cc. of water; (4) two cc. of extract and 0.6 cc. of 2% magnesium chloride solution.

Time in minutes	Cc. of carbon dioxide evolved 1	2	3	4
55	..	0.281	0.217	0.352
105	..	.576	.523	0.814
145	0.00	.857	.814	1.221

The magnesium chloride has an accelerating effect on the reaction, while the acetic aldehyde has practically none.

The Co-ferment in Banana Extract Diffuses through a Collodion Membrane.—Some ripe banana extract and a few drops of toluene were placed in a collodion dialyzing bag and the latter immersed in a large beaker of water. After dialyzing for two days, the liquid outside, of the bag was concentrated in an evaporating dish on the steam-bath to the original volume of the extract. The activities of the concentrated liquid, the contents of the dialyzing bag, and the original banana extract were determined in the usual way. Two cc. of yeast apo-zymase mixture (prepared as in the previous experiments) was added to each of a series of respiration flasks containing the following material: (1) two cc. of water; (2) two cc. of the contents of the dialyzing bag after

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[4] Euler and Myrback, *Z. physiol. Chem.*, 133, 260 (1924).

dialysis; (3) two cc. of concentrated liquid from outside the bag; (4) two cc. of the original banana extract.

Time *in minutes*	*Cc. of carbon dioxide evolved* 1	2	3	4
30	0.03	0.04	0.28	0.29
60	.06	.06	.53	.55
90	.06	.06	.63	.68

The values in columns 3 and 4 show that practically all of the co-ferment diffused through the collodion membrane.

Other Enzymes Belonging to the Glycolysis Chain. Phosphatase.—To test for the presence of phosphatase, a few drops of toluene, 2 cc. of a 4% sodium hexose diphosphate solution, and 5 cc. of water were added to 23 g. of ripe banana pulp, and the mixture ground in a mortar. Twenty cc. of a 6% trichloroacetic acid solution was added to the mixture and stirred, to destroy enzymes and precipitate proteins, and then made up to 250 cc. volume with water. After the mixture thus prepared had stood overnight, it was filtered and the inorganic phosphorus determined by Martland and Robison's modification of Briggs' method.[5] Two cc. of the filtrate contained 0 057 mg of inorganic phosphorus.

Another lot of pulp (24 g.), hexosc diphosphate, toluene and water, similar to that above, was prepared and allowed to stand overnight (eighteen hours) before adding the trichloroacetic acid, etc., so as to permit any phosphatase present to act on organic phosphates. Two cc. of this filtrate contained a much larger amount of inorganic phosphorus, 0.208 mg:, thereby showing the presence of phosphatase

In a similar way the banana extract was also found to contain phosphatase, showing this enzyme to be present in a soluble form

Phosphatese.—To see whether any phosphoric acid esterifying enzyme was present in the banana, 20 g. of pulp was ground with a few drops of toluene, 2 cc. of 0.66 *M* sodium phosphate and 5 cc. of water (P_H of resulting mixture about 5.8). To determine the amount of inorganic phosphorus present, 20 cc. of 6% trichloroacetic acid were added, the mixture made up to 500 cc. with water and filtered. One cc. of this filtrate contained 0.094 mg. of inorganic phosphorus. A similar preparation which was allowed to stand eighteen hours before adding the trichloroacetic acid gave practically the same amount of inorganic phosphorus per cc., 0.092 mg. The difference between these two values is practically within the limits of experimental error and hence cannot be taken as evidence for the presence of any phosphorylating enzyme in the banana. The authors, however, do not wish to state that any enzyme of this kind is absent, but rather that possibly the method used in testing for its presence may not have been suitable.

Carboxylase.—To test for carboxylase banana pulp was ground with 0.66 *M* sodium phosphate solution, P_H of mixture about 6.4, and equal amounts of the mixture were placed in each of two respiration flasks. To one sodium pyruvate was added and to the second an equal volume of water. In two hours the flask containing the pyruvate gave 2.62 cc. of carbon dioxide, while the flask to which water had been added gave off only 0.7 cc., showing therefore the presence of this enzyme. Water extracts and banana juice were only slightly active with respect to this enzyme.

The authors desire to express their thanks to the United Fruit Company for their financial aid in this work.

Summary

An aqueous extract of crushed banana pulp contains material which activates the glycolytic action of yeast apo-zymase.

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[5] Martland and Robison, *Biochcm. J.*, **20**, 847 (1926).

Pressed juice from banana pulp also contains this activator.

The aqueous extract may be heated to boiling for a few minutes without loss of its activating property, but when evaporated to dryness on the steam-bath at PH 6.4, it is rendered inert.

The glycolytic activator is more resistant to acid (PH 1) than to alkali (PH 9.4).

The activator passes through a collodion membrane on dialysis.

The effect of the activator, in the crude extract, on yeast apo-zymase is much less than that of yeast cozymase.

The effect of the activator on yeast apo-zymase is increased by small amounts of magnesium chloride, but hardly at all by acetic aldehyde.

The extract from the banana pulp also contained phosphatase and carboxylase.

NEW YORK CITY

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on the Rearrangement of Tertiarybutylmethylcarbinol (Pinacolyl Alcohol). I

BY FRANK C. WHITMORE AND H. S. ROTHROCK[1]

In spite of the large amount of work on pinacolyl alcohol, its dehydration products and its halides, the subject is still confused. This is shown by the fact that the fourth edition of Beilstein's "Handbuch" gives the halides the tertiary structure, $(CH_3)_2CXCH(CH_3)_2$, corresponding to a complete rearrangement, while the supplement to the fourth edition gives the structure, $(CH_3)_3CCHXCH_3$.

In the present work the chloride has been prepared from pinacolyl alcohol and saturated aqueous hydrochloric acid at $-10°$. The product reacted with moist silver oxide to give the rearranged product dimethylisopropylcarbinol. A bromide was prepared from pinacolyl alcohol. This was studied by the freezing point method[2] and was found to consist of about 90% of the rearranged tertiary bromide, $(CH_3)_2CBrCH(CH_3)_2$. The composition of the impure bromide was not changed by heating for sixteen hours at 125°. Hydrolysis experiments[2,3] also indicated that the mixture was about 90% tertiary.

The dehydration of *tert.*-butylmethylcarbinol was studied. Attempts to dehydrate the boiling alcohol by means of traces of benzene sulfonic acid and iodine failed. Dehydration of the alcohol with oxalic acid gave tetra-

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. Most of this work was done at Northwestern University in 1928–1929.

(2) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

(3) Delacre, Bull. *soc.* chim., [4] 1, 575, 978 (1907).

methylethylene and *unsym.*-methylisopropylethylene in the ratio 5:2. The fraction boiling at 65–67° observed by other workers[4] was shown to be a mixture of these olefins. By heating the —OMgBr derivative of the alcohol to 250–300°, a 3:2 mixture of the same olefins was obtained.6 Dehydration of the alcohol with iodine in a sealed tube at 140° gave a 6:1 mixture. When the acetate of pinacolyl alcohol was decomposed at about 300°, *tert.*-butylethylene was formed with only small amounts of rearranged products. This recalls the formation of the unrearranged olefin from the xanthate of pinacolyl alcohol.[6]

The alcohol itself has been found to be stable to long heating at 200°, in spite of suggestions in the literature that it undergoes rearrangement on repeated distillation.?

Experimental

The pinacolyl alcohol, b. p. 116.5–121° (740 mm.), was obtained by the action of acetaldehyde with *tert.*-butylmagnesium chloride. The yield was 28% bayed on the tertiary butyl chloride used. The alcohol was also made by reducing pinacolone,[8] with moist ether and sodium. The yields of material of b. p. 117–121" and m. p. 1.0–2.5". were about 70%.

Stability of Tertiarybutylmethylcarbinol and its Acetate to Heat.—The freezing point constant of the alcohol was found to be 5.6. Two duplicate sealed tubes containing samples of the alcohol, m. p. +1°, and filled with carbon dioxide, were heated at 200°. The first tube was cooled and opened after eighteen hours and the second after forty-eight hours. The freezing points of the two samples were —1.5 and —2.0°.[2] Mixed melting point determinations with unheated samples of the alcohol showed no depression. A sample of the alcohol of m. p. 1.6° was refluxed with protection from atmospheric moisture for forty-one hours. Its melting point was then found to be 1.4". These experiments indicate that the thermal decomposition of the alcohol was very slight.

The acetate of *tert.*-butylmethylcarbinol, b. p. 141.2–141.4" (740 mm.), was prepared by means of acetyl chloride. Five grams of the acetate was heated in *a* sealed tube at 160–170° for one hundred and forty-four hours. The product was heated for eighteen hours with alcoholic potassium hydroxide and worked up. About 3 g. of material boiling at 119–120° was recovered. Treatment with phenyl isocyanate gave the phenylurethan of *tert.*-butylmethylcarbinol, m. p. 77.5–78.5".

When 24 g. of the acetate was distilled over porous tile in a Pyrex tube heated in an electric furnace at about 300°, the product amounted to 8 g. of material of which 5 g. on refractionation boiled at 40–43.5° (740 mm.), a yield of *tert.*-butylethylene of about 35%. The olefin was oxidized with permanganate to trimethylacetic acid, which was identified by its odor and by conversion to the silver salt containing 51.7% silver (calcd. 52.1%).

Halides Obtained from Tertiarybutylmethylcarbinol

1. The Chloride.—Concentrated C. P. hydrochloric acid was cooled to —10° and saturated with hydrogen chloride gas. To 100 g. of this acid in a tube was added 20 g. of the carbinol, the tube was sealed and allowed to stand with occasional shaking

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(4) Zelinsky and Zelikow, *Ber.*, 34, 3248 (1901); Nybergh, "Hyllningsckrift tillagnad Ossian Aschan," 1920, pp. 98-102; *Chemical Abstracts*, 16, 2110(1922).

(5) Whitmore and Houk, THIS JOURNAL, 64, 3714(1932).

(6) Fomin and Sochanski, Ber., 46, 244 (1913).

(7) Van Risseghem, *Bull soc chim. Belg.*, 30, 8 (1921).

(8) "Organic Syntheses," 1925, Vol. V, pp. 87, 91.

(care!) at room temperature The solution was at first red and homogeneous. After a few hours a violet upper layer separated. This gradually increased for five days. It was then removed and washed with concd. hydrochloric acid and twice with water. The violet color disappeared during the latter treatment. The weight of the crude chloride was 24 g.

A suspension of washed silver oxide (from 35 g. of silver nitrate) in 400 cc. of water was treated with 20 g. of the chloride and allowed to stand with shaking at room temperature for four days. The mixture was extracted with ether and the extract was fractionated. A small amount of olefin boiling at 70–80° was obtained. The main fraction boiled at 116–117.5° (738 mm.). This was treated with phenyl isocyanate. No product soluble in hot ligroin (phenylurethan of pinacolyl alcohol) was obtained. Crystallization of the product from alcohol gave diphenylurea, m. p. 235°, thus indicating that the alcohol formed by the silver oxide treatment was a tertiary alcohol. No *tert.*-butylmethylcarbinol was regenerated. This indicates that the chloride obtained from pinacolyl alcohol and cold hydrochloric acid is the rearranged tertiary chloride. A blank experiment with 3-chloropentane and silver oxide under like conditions gave no reaction.

2. The Bromide.—(a) Fifty grams of the carbinol was cooled with ice and treated with dry hydrogen bromide until saturated. The mixture turned red. After standing for two days at 0°, the saturation with hydrogen bromide was repeated. This was repeated twice more. Meantime an aqueous layer had separated. This was removed, the treatment with hydrogen bromide was repeated and the mixture was heated for three hours on the steam-bath under a reflux condenser. The bromide was then separated and distilled under reduced pressure. The product of b. p. 88–90" (200 mm.) and m. p. 6.6"[9] weighed 68 g.

(b) For purposes of comparison dimethylisopropylcarbinyl bromide, b. p. 86–89' (180 mm.), m. p. 13.5°,[10] was prepared by the action of hydrobromic acid on dimethylisopropylcarbinol, b. p. 116–120° (740 mm.), obtained in 40% yield by the action of acetone with isopropylmagnesium bromide. The melting point of 13.5° was obtained only after repeated fractional crystallizations.

(c) Freezing point determinations were taken on mixtures of the bromide prepared from *tert.*-butylmethylcarbinol (m. p. 6.6°) and that from dimethylisopropylcarbinol (m. p. 9.8°) made in the ratios 5:2 and 1:1. These were 7.4 and 8.5°, respectively, indicating that the two materials contained mainly the same bromide.

A mixture of 4.55 g. of dimethylisopropylcarbinyl bromide, m. p. 9.8°, with 0.389 g. of *tert.*-amyl bromide, b. p. 106.5–107" (735 mm.), froze at 2.3°, thus indicating a molecular lowering of 13 If the true melting point of this bromide is 15°, the bromide made from *tert.*-butylmethylcarbinol and freezing at 6.6° contains about 0.84 mole of impurity in 1000 g. of pure bromide and thus contains about 90% of the tertiary bromide, $(CH_3)_2CBrCH(CH_3)_2$.

(d) A sample of the bromide of m. p. 6.6° prepared from *tert.*-butylmethylcarbinol was heated in a sealed tube at 125° for sixteen hours. The melting point was then 5.6°. If any unstable bromide had changed to the tertiary bromide, the melting point would have been raised.

(e) Weighed samples of dimethylisopropylcarbinyl bromide were shaken with distilled water and the water layers were titrated for bromide. In sixty-five minutes, 97% of the bromine in the bromide appeared as hydrogen bromide. Longer shaking gave no increase in this value.

In a similar way samples of the bromide of m. p. 6.6° were hydrolyzed by cold water to give 91–92.5% of the total bromine as hydrogen bromide, indicating a corresponding content of the tertiary bromide $(CH_3)_2CBrCH(CH_3)_2$. The nature of the stable diffi-

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(9) Couturier, *Ann chim phys.*, [6] 26, 433 (1892); Delacre, *Bull soc chim*, [31 35, 348 (1906)

(10) Zelinsky and Zelikow, *Ber*, 34, 2858 (1901).

cultly hydrolyzable bromide forming less than 10% of the product has not yet been determined

Dehydration of Tertiarybutylmethylcarbinol

(a) Refluxing 30 g. of the carbinol (b. p. 118–120) with 0.1 g. of benzene sulfonic acid for 120 hours gave less than 0.5 g. of material boiling below 85°. A total of 27 g. of the carbinol was recovered unchanged.

(b) Dehydration of the carbinol with anhydrous oxalic acid gave a distillate boiling at 55–65°. When dried and carefully fractionated,'' the chief fractions boiled at 740 mm. at 55–59' and 69.5–72° with only very small intermediate fractions. These were found in the ratio 2:5 and were the *unsym.*-methylisopropylethylene and tetramethylethylene reported by other workers. When careful fractionation was employed there was no indication of the 65–67° material reported by Zelinsky and Zelikow and by Nybergh.[4]

(c) The —OMgBr compound of the carbinol was made by treating a dry ether solution of 30 g. of the latter with the calculated amount of titrated ethylmagnesium bromide solution. The ether was evaporated and the residue was heated in an oil-bath. When the bath reached 170°, a distillate came over at 33.5–34.5°. Tests with bromine solution failed to indicate any unsaturated material (boiling point of *tert.*-butylethylene, 41°). The bath was then raised to 250° and then to 340°. A total of 20 g. of material boiling at 55–65' was obtained. Three careful fractionations of this material gave 4.5 g., b. p. 54–59°, and 6.5 g., b. p. 67–72". No indication of *tert.*-butylethylene was detected.

(d) All attempts to dehydrate the carbinol by refluxing with iodine failed. Finally 19 g. of tertiarybutylmethylcarbinol and 1 g. of iodine were heated in a sealed tube at 140". After eight hours two layers had formed. These did not change after heating for eight hours longer. The lower (water) layer amounted to 4 g. The upper layer was dried with sodium and fractionated carefully at 732 mm. The chief fractions were 1.4 g., b. p. 61.5–67°, and 8 g., b. p. 69–72.5". Thus about 86% of the product was tetramethylethylene.

Summary

1. The stabilities of *tert.*-butylmethylcarbinol and its acetate have been studied. At high temperature, the acetate gives *tert.*-butylethylene without rearrangement.

2. The chloride and bromide obtained from the carbinol consist almost entirely of rearranged products.

3. A variety of means of dehydration of the carbinol give only tetramethylethylene and *unsym.*-methylisopropylethylene without any third product.

STATE COLLEGE, PENNSYLVANIA

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(11) Whitmore and Lux, THIS JOURNAL, 54, 3451 (1932)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE RICE INSTITUTE]

Imidazole Derivatives of Barbituric Acid

BY MILLARD S. TAGGART AND G. HOLMES RICHTER

Following the discovery of Fisher and Mehring in 1903 that 5,5-diethylbarbituric acid was an excellent hypnotic, chemical and medicinal interest in the barbituric acid derivatives has become very great.

The known derivatives of barbituric acid are, in general, the aliphatic and aromatic substituted compounds. The heterocyclic derivatives of barbituric acid have not received the chemical attention that they deserve. The purpose of this investigation was to prepare several heterocyclic derivatives of barbituric acid. Among the possibilities in this field, imidazole derivatives were considered to be of outstanding interest. This was suggested by the known physiological importance of simple imidazole compounds such as histidine, histamine, pilocarpine, etc.

The method of preparation was to condense 4(or 5)-chloromethylimidazole with monoalkylated malonic esters and subsequently to condense these compounds with urea. In this manner 5-*n*-butyl-5-[4(or 5)-imidazolemethyl]-barbituric acid and 5-isoamyl-5-[4(or 5)-imidazolemethyl]-barbituric acid were prepared. The 4(or 5)-chloromethylimidazole was prepared by the method of Pyman[1] with some modifications suggested by Koessler and Hanke.[2]

Experimental Part

Acetone Dicarboxylic Acid.—This material was prepared according to the directions given in "Organic Syntheses" (Vol. V, p. 5) except that the excess sulfuric acid was not removed as this was one of the reagents in the following synthesis.

Diisonitrosoacetone.—The crude material obtained above was converted into diisonitrosoacetone by means of the reaction described by Pechmann.[3]

Diaminoacetone Chlorostannite.—This material was prepared by the reduction of diisonitrosoacetone according to the method described by Kalischer.[4]

Diaminoacetone Hydrochloride.—The diaminoacetone chlorostannite was decomposed by means of hydrogen sulfide in the manner described by Koessler and Hanke.[2] Frequently in this treatment a colloidal suspension of the tin sulfide is obtained; if this occurs, dilution with distilled water will cause the sol to coagulate.

2-Thiol-4(or 5)-aminomethylimidazole Hydrochloride.—The diaminoacetone hydrochloride was condensed with sodium thiocyanate in the manner described by Pyman.[1]

4(or 5)-Hydroxymethylimidazole Picrate.—Following the method of Pyman this compound was prepared by the oxidation of 2-thiol-4-aminomethylimidazole hydrochloride and subsequent treatment of the material with picric acid. In this connection it was noted that a sodium-free picrate could be conveniently obtained by omitting the neutralization with dry sodium carbonate as recommended by Koessler and Hanke. This is made possible by the relative insolubility of the picrate in water.

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(1) Pyman, *J. Chem. Soc.*, 99, 668 (1911).

(2) Koessler and Hanke, THIS JOURNAL, 40, 1717 (1918).

(3) Pechmann, *Ber.*, 19, 2465 (1886).

(4) Kalischer, *ibid.*, 28, 1519 (1895).

4(or 5)-Hydroxymethylimidazole Hydrochloride.—The above picrate was decomposed by hydrochloric acid and the picric acid extracted with benzene.

4(or 5)-Chloromethylimidazole Hydrochloride.—This material was prepared by the action of phosphorus pentachloride on the above alcohol according to the directions of Pyman.

Condensation of 4(or 5)-Chloromethylimidazole with Ethyl *n*-Butylmalonic Ester.—The apparatus was dried by a stream of dry air heated to 150°. After cooling to room temperature 200 cc. of a special grade of absolute alcohol was distilled into the reaction flask and 4 6 g. of clean sodium dissolved in it. The n-butylmalonic ester was added, and the excess alcohol removed by distillation; 15 g. of the chloromethylimidazole hydrochloride dissolved in alcohol was then added over a period of several hours. The solution was then refluxed for two hours and the alcohol distilled off in *vacuo.* The material was transferred to a separatory funnel and treated with 150 cc. of approximately 5% hydrochloric acid and extracted with ether several times. The aqueous solution was then made alkaline with sodium carbonate and extracted with ether. The ether solution was dried over anhydrous sodium sulfate, and the ether removed in *vacuo;* a glassy solid was obtained which weighed 16.3 g. (55.9%). Better yields can be obtained by carrying the reaction out at lower temperatures and for shorter times.

5-n-Butyl-5[4(or 5)-imidazolemethyl]-barbituric Acid.—Ninety cc. absolute alcohol was placed in a Pyrex tube closed at one end and 3.8 g. of sodium was dissolved in it; 4.86 g. of urea and 16 g. of the substituted malonic ester were then added, and the tube sealed off and heated for twenty-two hours with steam. It is essential that the substituted malonic ester be thoroughly dried over phosphorus pentoxide before use. At the end of this period the tube was opened and the contents were evaporated to near dryness and then dissolved in 80 cc. of water. The solution was extracted twice with ether to recover the unchanged malonic ester, and then very carefully treated with dilute acetic acid. At first considerable tar separated which was immediately removed; a fine crystalline material gradually separated from the filtrate on standing overnight. This material was treated with norite and recrystallized from dilute alcohol, giving snowwhite crystals of indefinite melting point The material decomposed around 290°, and no true melting point was obtained.

Anal. Calcd. for $C_{12}H_{16}O_3N_4$: N, 21.21. Found: N, 21.72.

4(or 5)-Imidazolemethyl-isoamylmalonic Ester.—The reaction was carried out in a similar fashion to that for the preparation of the corresponding butyl compound. It differed, however, in the following details. The chloride in 120 cc. of alcohol was added over a period of two hours and the temperature during the addition was 95° The materials were refluxed for one-half hour after the addition. The mixture was worked up as was the *n*-butylmethylimidazole malonic ester, the yield being 52.3%.

5-Isoamyl-5-[4(or 5)-imidazolemethyl]-barbituric Acid.—The condensation with urea was essentially the same as that described for the preparation of the n-butyl derivative. The tube was heated for ten hours, and the product obtained in the manner outlined above. Like the lower homolog, the material showed no tendency to melt but decomposed with considerable charring.

Anal. Calcd. for $C_{13}H_{18}O_3N_4$: N, 20.15. Found: N, 20.32.

An attempt to prepare the corresponding allyl compound met with little success.

Summary

The synthesis of substituted barbituric acid derivatives in which one of the groups in the 5-position is a methylimidazole residue is described.

HOUSTON, TEXAS

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[Contribution from the Chemical Laboratory of the University of North Carolina]

Some Reactions of Tetra-para-tolyltin

By R. W. Bost and H. R. Baker

The reactions of tetraphenyltin have been reported by Bost and Borgstrom.[1] Smith and Kipping[2] have studied the reaction of tetra-p-tolyltin with two moles of bromine, whereupon ditolylstannic dibromide was obtained.

This work was undertaken to determine whether tetra-p-tolyltin could be used to prepare para substitution products of toluene free from the ortho isomers and also whether the side chain entered into any of these reactions. The formation of pure *p*-nitrotoluene is noteworthy in this connection. Since the substitution of a methyl group in the benzene ring enhances the activity of the ring, tetra-p-tolyltin should be very reactive toward entering substituents. Its action with iodine bears out this prediction. Tetraphenyltin does not react appreciably under similar conditions. Other reagents also show this difference in reactivity, although less pronounced. In this work tetra-p-tolyltin was studied with the halogens, alkyl halides, acyl halides, mineral acids and sulfur.

The tetra-p-tolyltin was prepared by the action of stannic bromide on *p*-tolylmagnesium bromide in 52% yields. Pfeiffer[3] who first prepared it obtained only a 24.8% yield. It is a white crystalline substance melting at 230°.

Action of Halogens

Chlorine.—To 9.66 g. of tetra-p-tolyltin in a 250-ml. flask cooled in ice and attached to a reflux condenser, was slowly added a cold solution of 5.68 g. of chlorine in 150 ml. of chloroform. After refluxing for one hour on a steam-bath, the solvent was removed by distillation. The residue was transferred to a small flask and distilled. An 85% yield of p-chlorotoluene was obtained, b. p. 162–163". m. p. 7°. No isomeric products were obtained. The reaction was repeated at room temperature and also in boiling carbon tetrachloride. In all cases only p-chlorotoluene was obtained.

Bromine.—The above experiment was repeated using 9.66 g. of tetra-p-tolyltin and adding 12.78 g. of bromine dropwise. Much heat was evolved with the formation of a colorless liquid, After gently refluxing for an hour a 90% yield of *p*-bromotoluene was obtained upon distillation, b. p. 184–185°, m. p. 28°. No isomers were obtained.

Iodine,—To 9.66 g. of tetra-p-tolyltin in a 500-ml. flask was added slowly a cold solution of 20.3 g. of iodine in carbon tetrachloride. The iodine solution was decolorized as fast as added until about one-half had been added. After refluxing for an hour, the solvent was removed and finally the p-iodotoluene; yield 81%, b. p. 210–211. m. p. 35°. No isomers were obtained.

Action of Alkyl Halides

Tetra-*p*-tolyltin in 0.02-mole portions was heated under reflux for thirty-six hours

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[1] Bost and Borgstrom, This Journal, 51, 1922 (1929).

[2] Smith and Kipping, J. Chem. *Soc.*, 103, 2049 (1913).

[3] Pfeiffer *Z. anorg.* Chem., 68, 104 (1910).

with a slight excess of ethyl and isopropyl bromides, respectively. No reaction occurred and the products were recovered unchanged.

Tert-butyl Bromide.--9.66 g. of tetra-p-tolyltin was refluxed for eighteen hours with 10.96 g. of tert-butyl bromide. The products of reaction consisted of some unused tetra-p-tolyltin, hydrogen bromide, isobutylene, traces of toluene and some unused halide.

Action of Acyl Halides

Acetyl Chloride.—9.66 g. of tetra-p-tolyltin was refluxed on a steam-bath with 6.28 g. of acetyl chloride for twenty-four hours. A reaction occurred but no definite substance could be identified. No methyl tolyl ketone was obtained.

Benzoyl Chloride.—S.66 g. of tetra-*p*-tolyltin and 11.24 g. of benzoyl chloride were refluxed for six hours on a steam-bath. The cold product was extracted with dilute sodium hydroxide to remove any benzoic acid. The mass was extracted with ether, which yielded a tarry residue upon evaporation. When the residue was recrystallized from petroleum ether, a 5% yield of p-tolyl phenyl ketone was obtained, m. p. 59°.

Benzene **Sulfonyl** Chloride.—9.66 g. of tetra-p-tolyltin and 7.5 g. of benzene sulfonyl chloride were heated in a sealed tube at 200° for five hours. The product was extracted with benzene, which yielded a dark residue. The latter was recrystallized from acetone. An 84.3% yield of *p*-tolyl phenyl sulfone was obtained, m. p. 124°. No definite product could be isolated when the reaction was carried out under reflux for twenty-four hours.

Action of Acids

Nitric Acid.—To 9.66 g. of tetra-p-tolyltin in a flask surrounded by ice and attached to *a* reflux condenser was added dropwise 5 ml. of concentrated nitric acid. A violent action soon occurred, evolving much heat. After the reaction had subsided, the mixture was heated on a steam-bath for thirty minutes, the product washed with water, and extracted with hot alcohol. The residue from the alcohol extract was recrystallized from dilute alcohol. Long pale yellow needles of p-nitrotoluene separated, yield 85%, m. p. 55". No ortho isomer was found in the reaction.

Sulfuric Acid.—The above experiment was repeated using concentrated sulfuric acid instead of nitric acid. A vigorous reaction occurred. The mixture was heated on a steam-bath for one hour and distilled. A 94% yield of toluene was obtained, b. p. 110–111°. A similar yield was obtained at room temperature.

Action of Sulfur

p-Ditolyl **Disulfide.**—9.66 g. of tetra-p-tolyltin and 1.92 g. of sulfur (three equivalents were heated at 170° in a sealed tube for ten hours. The reaction product was extracted with ether. A light brown oil was obtained which gave a 45% yield of p-ditolyl disulfide upon distillation, b. p. 298–300°, m. p. 44–5°.

3,7-Dimethylthianthrene.—The reaction was repeated using five equivalents of sulfur and heating the tube at 190° for eight hours. The extract gave a product which upon purification gave an 80% yield of 3.7-dimethylthianthrene, m. p. 123".

Summary

Tetra-p-tolyltin reacts with halogens to form the corresponding aryl halides, with nitric and sulfuric acids to form *p*-nitrotoluene and toluene, respectively, and with sulfur under different conditions to form *p*-ditolyl disulfide and 3,7-dimethylthianthrene. No isomers were obtained with the halogens or nitric acid. Reactions of acyl and alkyl halides are less marked.

CHAPEL HILL, NORTH CAROLINA

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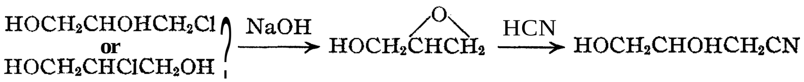
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

The C_4-Saccharinic Acids. VI. Further Attempts to Prepare 2,2'-Dihydroxyisobutyric Acid. 2,3-Dihydroxybutyric Acid Lactone from Glycidol. The Preparation of the Two Iodohydrins of Glycerol[1]

BY J. W. E. GLATTFELD AND ROSALIND KLAAS

In previous work in this Laboratory[2] it was found that 2,2'-dihydroxyisobutyric acid could not be prepared by the treatment of β-glycerolchlorohydrin with sodium cyanide followed by hydrolysis of the nitrile thus obtained. Pure β-glycerolchlorohydrin gave the same product as did pure α-glycerol chlorohydrin, namely, 2,3-dihydroxybutyric acid lactone (hereafter called, for the sake of brevity, "2,3-acid lactone"). In explanation of this fact it was suggested that both chlorohydrins under the experimental conditions used yielded glycidol, which then added hydrogen cyanide to form the nitrile of the 2,3-acid almost exclusively. This paper reports the results of a study which was undertaken partly to test this hypothesis.

The reaction of glycidol with hydrogen cyanide was carried out under various conditions; in each experiment, with one exception, the only product that was isolated and identified was the 2,3-acid lactone, in a yield varying from 25 to 50%. The one exception was an experiment with benzene as the solvent in which the chief product of the reaction was 3-hydroxyisocrotonic acid lactone.[3] Other products of the reaction consisted of dark-colored tars, probably polymers of glycidol, and of acids of high molecular weight. The results of the study thus confirm the hypothesis that the mechanism of the reaction of the monochlorohydrins of glycerol with sodium cyanide is as follows:



$$\left.\begin{array}{l}HOCH_2CHOHCH_2Cl\\ \text{or}\\ HOCH_2CHClCH_2OH\end{array}\right\} \xrightarrow{NaOH} HOCH_2\overset{O}{\widehat{CHCH_2}} \xrightarrow{HCN} HOCH_2CHOHCH_2CN$$

On the basis of this theory, it is the alkali resulting from the hydrolysis of the cyanide which causes the formation of the glycidol. In the further attempt to prepare 2,2'-dihydroxyisobutyric acid from β-chlorohydrin, the presence of alkali was avoided by the use of cuprous cyanide[4] and of mercuric cyanide.[5] With the former, a small amount of acid of high molecular weight was obtained, while with the latter only tars and resins resulted.

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(1) This article is constructed from a dissertation presented by Rosalind Klaas in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Glattfeld, Leavell, Spieth and Hutton, THIS JOURNAL, **53**, 3164 (1931).

(3) It is interesting to note that 3-hydroxyisocrotonic acid lactone is also formed in the preparation of the 2'3-acid from glycerol chlorohydrin and sodium cyanide in water or alcohol solution.[2] The exact source of this by-product has not yet been ascertained, but in view of the data in the experiment mentioned above, it must be formed at some time after the glycidol is generated from the chlorohydrin.

(4) Tschelinzeff and Schmidt, Ber., 62, 2211 (1929).

(5) Guillemard. Ann. *chim. phys.*, [8] 14, 383 (1908); Bull. *soc. chim.*, [4] 1, 532 (1907).

The diacetyl and dibenzoyl derivatives of β-glycerol chlorohydrin[6] were also used in the attempt to prepare 2,2′-dihydroxyisobutyric acid, inasmuch as these cannot readily form oxygen ring compounds. It was shown, however, that they are rather inactive substances, for they failed to react with magnesium with ether as the solvent. Even metallic sodium did not remove the chlorine atom from the dibenzoyl compound dissolved in benzene when the mixture was heated for fifteen hours. The diacetyl derivative, on the other hand, was decomposed by sodium. However, the reaction in which the diacetyl compound was treated with ethyl chloroformate and 4% sodium amalgam,[7] with subsequent hydrolysis of the product formed, failed to yield any acid which could be identified as 2,2′-dihydroxyisobutyric acid.

A few experiments on the oxidation of pentaerythritol were next carried out. Just[8] was able to obtain isobutyric acid from 2,2-dimethylpropanediol (1,3), according to the equation

$$(CH_3)_2C(CH_2OH)_2 \xrightarrow{KMnO_4} (CH_3)_2C(COOH)_2 \xrightarrow{Heat} (CH_3)_2CHCOOH + CO_2$$

It was hoped that under suitable conditions an analogous reaction would take place with pentaerythritol which would yield 2,2′-dihydroxyisobutyric acid. Dilute solutions of potassium permanganate and of barium permanganate were employed as oxidizing agents in neutral and in acid media. The reaction was in each case vigorous, even at 5°, but the chief product of the oxidation appeared to be carbon dioxide. These experiments with pentaerythritol are only preliminary, and it is planned to study this reaction further.

Since it was thought that β-glycerol iodohydrin might prove a possible source material for the acid desired, its synthesis was effected. The ***a***-

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(6) These compounds were prepared in this Laboratory by G. W. Schimpff (S M. Dissertation, University of Chicago, 1930). The diacetyl compound was obtained by refluxing 1 mole of pure β-glycerol chlorohydrin (K_{50} = 0.92. See Smith, *Z. physik. Chem.*, 92, 717–740 (1918); 94, 691–738 (1920)) with 4 moles of acetic anhydride for eight hours, removing the acetic acid and excess anhydride by distillation at atmospheric pressure, and boiling the residue for four hours with 2 moles of acetic anhydride. After the removal of acetic acid and excess anhydride as before, the residue was heated with water in order to remove unchanged 8-glycerol chlorohydrin. The aquedus layer was discarded and the residue fractionated. A fraction which boiled at 107–109° at 5–6 mm. with oil-bath at 132–134° was redistilled; it gave a product which boiled at 101–102° at 4 mm. with oil-bath at 114–116°; yield 51%.

Anal. Subs., 0.2528, 0.2528: 12.92 cc., 13.00 cc. of 0.0991 *N* $AgNO_3$. Calcd. for $C_7H_{11}O_4Cl$: Cl, 18.23 Found: Cl, 17.96, 18.07.

The dibenzoyl derivative was prepared by mixing at 0° a solution of 1 mole of pure β-glycerol chlorohydrin in 2.5 moles of pyridine with a solution of 2 moles of benzoyl chloride in 6 moles of chloroform. After the mixture had been allowed to stand at room temperature for twenty-four hours, it was shaken with 3 volumes of a mixture of equal volumes of water and ether. The ether extract was washed successively with dilute sulfuric acid, sodium bicarbonate solution, and water, and then dried over anhydrous sodium sulfate. After the removal of the ether, the residue was fractionated. The fraction which distilled at 212–224° at 4 mm. was redistilled; it gave a product which boiled at 210–211° at 1.5 mm.; yield 39%.

Anal. Subs., 0.2868, 0.2907: 9.40 cc., 9.50 cc. of 0.0991 N $AgNO_3$. Calcd. for $C_{17}H_{15}O_4Cl$: Cl, 11.13. Found: Cl, 11.51, 11.48.

(7) Würtz, *Compt. rend.*, 68, 1298 (1869). *Cf.* Calvery, THIS JOURNAL, 48, 1009 (1926).

(8) Just, *Monatsh.*, 17, 76 (1896).

glycerol iodohydrin[S] has been known for some time, but the β-iodo derivative is new to the literature. Since the methods of preparation used by previous workers were long and tedious, a new procedure was developed for the preparation of the alpha compound. The same procedure was then adapted to the preparation of the beta compound. The details are given below.

This paper also reports some work on the reaction of β-iodohydrin with sodium cyanide. The experiments carried out gave rise only to the 2,3-acid and to sirupy materials that were not identified. Thus at the present time the results indicate that @-glyceroliodohydrin, like the β-chlorohydrin, gives the straight chain nitrile after reaction with alkali cyanides.

A method for the preparation of the 2,2′-dihydroxyisobutyric acid is still being sought in this Laboratory.

Experimental Part

Glycidol and Gaseous Hydrogen Cyanide.—Glycidol (boiling point 42–43° at 1.5 mm. with bath at 70°) was prepared from glycerol monochlorohydrin according to the method of Rider and Hill.[10] Anhydrous gaseous hydrogen cyanide was bubbled through 10 g. of glycidol until the gain in weight was 4.5 g. (3.7 g. calcd.). The solution was heated in a pressure bottle at 60–70° for twelve hours. After the excess hydrogen cyanide had been removed at reduced pressure, the sirup was dissolved in 100 cc. of water, and to the solution 21 g. of hydrated barium hydroxide was added. The mixture was heated on a steam-bath for thirty hours under a reflux condenser while a stream of nitrogen was bubbled through. After the removal of all but a trace of the barium ion by means of sulfuric acid and of the water by distillation at reduced pressure, there remained 13.7 g. of a very dark sirup. This was extracted repeatedly with small portions of boiling absolute ethanol in which the tarry material present was insoluble. After the removal of the alcohol at reduced pressure, the residue (weight 9.1 g.) was distilled at 4 mm. The first drop of distillate came at 128° with the bath at 172°, but practically all of the distillate (weight 3.5 g.) came at 140–146° with the bath at 185°. This boiling range and the phenylhydrazide (m. p. 109°) prepared from the acid, identified this material as 2,3-dihydroxybutyric acid lactone; yield, 25%.

Glycidol and a Benzene Solution of Hydrogen Cyanide.—To a solution of 5 g. of liquid hydrogen cyanide and 5 g. of glycidol in 13.5 g. of benzene, there were added a few crystals of potassiuin cyanide moistened with a drop of water. The mixture was allowed to stand for six days at room temperature. At the end of that time two layers had formed. The upper benzene layer was decanted and gentle suction was applied to the residue to remove all volatile constituents. The brown viscous sirup which remained was dissolved in 60 cc. of water, and 6 g. of anhydrous barium hydroxide added. The mixture was heated on the steam-bath under a reflux condenser in a stream of nitrogen until no more ammonia was evolved (forty-two hours). After the removal of the barium ion and of the water, the sirup was distilled at 2 mm. The distillate, which came over between 50 and 110° with the bath at 160–180°, weighed 2.7 g. Upon redistillation, 1.5 g. of a colorless liquid was obtained, which crystallized when chilled in a carbon dioxideacetone mixture and melted at 2° After redistillation the boiling point was 71° at 2.5 mm. with the bath at 125' and the melting point 5°. These are the con-

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(9) (a) Réboul, *Jahresb. Fortschritte Chem.*, 459 (1860); (b) Ltiders, German patent 291.541, 291.922 (1914); *cf. Schweiz. Apoth.-Ztg.*, **53**, 613 (1915); (c) Fischer and Pfähler, *Ber.*, **53**, 1606 (1920).

(10) Rider and Hill, Tars JOURNAL, **52**, 1521 (1930).

stants for 3-hydroxyisoaotonic acid lactone, which is thus shown to be the main product of the reaction under the conditions chosen for this experiment.

Glycidol and an Aqueous Solution of Hydrogen Cyanide.—A 500-cc. three-necked flask, fitted with a reflux condenser, a dropping funnel, and a mercury-sealed mechanical stirrer, was used in this experiment. A few crystals of potassium cyanide were added to a solution of 14.5 g. of liquid hydrogen cyanide in 30 cc. of water. The solution was warmed on the steam-bath to such a temperature that liquid dropped from the end of the condenser at the rate of thirty drops per minute. Twenty grams of glycidol was added with stirring during the course of two and a half hours. The heating and stirring of the solution were continued for three hours longer. After the removal of the excess hydrogen cyanide and part of the water by reduced pressure distillation, the residue was dissolved in 200 cc. of water, and 24 g. of anhydrous barium hydroxide added. The mixture was heated for thirty-six hours on the steam-bath under a reflux condenser in a stream of nitrogen. After the removal of the barium ion and of the water in the usual manner, there remained 28 g. of viscous brown sirup. This was combined with 14.5 g. of sirup similarly prepared from 10 g. of glycidol. The combined material was distilled at 3 mm. A 3-g. fraction was collected from 78 to 130°, and 24.1 g. from 130 to 154°. The residue was a dark glass-like substance, almost insoluble in water. Titration indicated that the larger fraction was 2.3-acid lactone, since it titrated 4.8% free acid and 85.9% lactone.[11] The yield of 2,3-acid lactone calculated on the basis of this analysis was 50%. The lactone was purified by conversion to the barium salt, removal of the barium, and distillation of the lactone. A sample titrated correctly for a dihydroxybutyric lactone (subs., 0.2013; calcd. 19.73 cc. of 0.1 *N* alkali; found, 19.20 cc.), and it gave a phenylhydrazide which melted at 109°.

Preparation of **α-Glycerol Iodohydrin.**—This compound was prepared by Lüders[9b] by shaking a-glycerol chlorohydrin with excess sodium iodide for many days. Fischer and Pfähler[9c] prepared it from isopropylidene-a-chlorohydrin by dissolving this compound in alcohol and heating it with sodium iodide in a sealed tube at 100° for three days. The method used in the present study was developed from the work done by Conant and Kirner[12] on the rate of transformation of chlorides into iodides.

A mixture which consisted of 23 g. of crude (*i. e.*. containing some *β*-) a-glycerol chlorohydrin (prepared from glycerol and hydrochloric acid), 35 g. of sodium iodide, and 200 cc. of acetone was introduced into each of two citrate of magnesia bottles and heated in steam for four hours. The sodium iodide used was dried in an oven at 110° for two hours and cooled in a desiccator. The acetone was boiled with lime and potassium permanganate for several days and then distilled through a 61-cm. fractionating column. The fraction which boiled at 56–56.5° was collected in a receiver carefully protected from moisture. The sodium chloride was removed from the cooled reaction mixture by suction filtration and washed with acetone until white (wt. 18.5 g., 75%). After the removal of the acetone at reduced pressure at 40°, the sirup was extracted with ether (which had been dried over anhydrous sodium sulfate) until the excess sodium iodide was white and powdery. The ether extracts were decanted, combined, washed with sufficient concentrated sodium thiosulfate solution to remove the iodine, and dried over anhydrous sodium sulfate. After the removal of the ether the residue was distilled. A large fraction (isopropylidene-a-iodohydrin, wt. 36 g., yield 37%) came at 75–78° at 5–6 mm. with the bath at 100–105°; and a 4-g. fraction was collected while the temperature of the bath was raised to 148°, with the temperature of the vapor rising rather rapidly to 115°. Distillation was then stopped, because the flask became filled with iodine vapors. The dark residue (wt. 28 g.), when seeded with a crystal of a-glycerol iodohydrin, set to a mass of crystals. The crystals were pressed between filter papers to

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[11] Glattfeld and Miller, THIS JOURNAL, 42, 2317 (1920).

[12] Conant and Kirner, *ibid.*, 46, 232 (1924).

remove adhering oils, dissolved in warm chloroform and precipitated with high boiling ligroin; weight **12.5** g., glistening, scale-like crystals, m. p. **47–47.5°**, yield **15%.** These retained a cream tint even after several recrystallizations.

Pure white crystals were obtained, however, by the hydrolysis of **isopropylidene-α-iodohydrin (36** g. fraction above). Into a mixture of this compound (which had been washed with sodium thiosulfate solution and water) with three times its weight of water there was introduced a drop of **5** *N* hydrochloric acid. The mixture was heated with vigorous shaking under a **reflux** condenser until the globules of oil disappeared. The cold solution was extracted with ether, and the extract dried over anhydrous potassium carbonate. After the evaporation of the ether, the clear viscous sirup set to a solid mass of crystals. In one experiment **28** g. was obtained from **65** g. of **isopropylidene-α-**iodohydrin. After two recrystallizations from a chloroform–ligroin mixture, the crystals melted at **48–48.5°.**

Anal. Subs., **0.1097, 0.1254: 5.49** cc., **6.29** cc. of **0.09973** *N* $AgNO_3$. Calcd, for $C_3H_7O_2I$: I, **62.85.** Found: **I, 63.34, 63.48.** This product was identical with that obtained under similar conditions from a sample of pure **α-glycerol** chlorohydrin (K_{50} = **9.5).**

Preparation of **β-Glycerol Iodohydrin.—Freshly** distilled pure @-glycerol**chloro**hydrin (K_{50} = **0.605, %** Cl = **31.46)** was used as the starting material. The procedure described above was used except that the time of heating was prolonged to twelve hours. The weight of sodium chloride that separated was **60%** of the theoretical. After the removal of the ether, the residue was fractionated at **2** mm. in order to remove unchanged **β-chlorohydrin.** The distillation was discontinued when a temperature of **108"** was reached, with the bath at **135".** Even though a stream of dry nitrogen was conducted through the apparatus during the distillation, the decomposition was marked. The drop of clear liquid adhering to the thermometer at the end of the distillation was transferred to a watch crystal and stirred. It quickly set to a mass of crystals. These were used to inoculate the dark viscous residue, which almost immediately became a thick crystalline mass. This was pressed on sheets of filter paper to remove the adhering dark oil; **15** g. of cream colored crystals was obtained from 45 g. of @-chlorohydrin, yield **18%.** These were dissolved in warm chloroform, and after the solution had cooled to **10°, 11** g. of fine, white needles was obtained; m. p. **52–53';** soluble in water, ethanol, chloroform, acetone, ether; insoluble in ligroin. When a few of the crystals were mixed with crystals of pure a-glycerol iodohydrin, the mixture turned at once to a soft paste. When small amounts of each type of crystals were introduced separately into a melting point tube and mixed by vibrating the tube with a file, the mixture melted from **32** to **45°.**

Anal. **Subs., 0.1216, 0.0552: 6.13** cc., **2.77** cc. of **0.09973** *N* $AgNO_3$. Calcd. for $C_3H_7O_2I$: I, **62.85.** Found: I, 63.80, 63.51.

Reaction of **β-Iodohydrin** with Sodium Cyanide.—Five grams of **β-glycerol iodo**hydrin and 1.21 g. of sodium cyanide were dissolved in a mixture of **25** cc. of **95%** ethanol and **4** cc. of water. The solution was heated under a **reflux** condenser for two hours. It was then acidified with **0.1** *N* nitric acid, and a solution of **4.21 g.** of silver nitrate in **50** cc. of water was slowly added. The purpose of this procedure was to replace the sodium iodide by sodium nitrate, which is far less soluble in ethanol than is sodium iodide. The silver iodide was removed by filtration. The water was removed *in vacuo,* and the residue extracted with ethanol. After the removal of the ethanol, the residue was dissolved in **50** cc. of water, and **2.1 g.** of anhydrous barium hydroxide added. The mixture was heated on a steam-bath for eighteen hours under a **reflux** condenser in a stream of nitrogen. After the removal of all but a trace of the barium ion and of the water, there remained a viscous sirup, from which a **phenylhydrazide**

which melted at 107.5–108.5° was prepared. When some of this material was mixed with crystals of the phenylhydrazide of 2,3-dihydroxybutyric acid (m. p. 109°), no depression in melting point was observed. It thus appears that 2,3-dihydroxybutyric acid had been formed in the reaction of the β-iodohydrin with sodium cyanide.

Summary

1. The addition of hydrogen cyanide to glycidol followed by hydrolysis of the addition product resulted in a 25–50% yield of 2,3-dihydroxybutyric acid lactone. Under certain conditions, 3-hydroxyisocrotonic acid lactone was formed.

2. Further attempts were made to prepare 2,2′-dihydroxyisobutyric acid from (a) β-glycerol chlorohydrin and heavy metal cyanides; (b) β-glycerol chlorohydrin diacetate, ethyl chloroformate and sodium amalgam; and *(e)* pentaerythritol by oxidation with barium or potassium permanganate. These attempts were unsuccessful.

3. a-Glycerol iodohydrin was prepared by a new procedure.

4. β-Glycerol iodohydrin was prepared and its melting point determined. The reaction of this compound with sodium cyanide in ethanol gave 2,3-dihydroxybutyric acid.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Dehydration of 2,2-Dimethylhexanol-1 and Related Tertiary Alcohols[1]

BY FRANK C. WHITMORE AND J. M. CHURCH[2]

An alcohol of the type, R_3CCH_2OH, can be dehydrated only with rearrangement. The purely aliphatic alcohols of this type which have been studied are tertiary-butylcarbinol,[3] tertiary-amylcarbinol[4] and 2-methyl-2-ethylbutanol-1.[4] In the present study a related alcohol with two methyl groups and a n-butyl group attached to the neo carbon has been dehydrated. This substance presented another opportunity to study the relative ease of migration of butyl and methyl groups. Meerwein[5] found that the butyl group migrated to a greater extent in the glycol containing two methyl and two butyl groups. A similar observation has been made by Krueger[6] in the case of two pinacolyl alcohols each containing two methyl and two butyl groups. In the present case in which there were two

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(1) See Whitmore, THIS JOURNAL, 54, 3274 (1932).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Cf. Whitmore and Rothrock, THIS JOURNAL, 54, 3431 (1932).

(4) Favorsky, J. Russ. *Phys.-Chem. Soc.*, 50, 43-80 (1918); *Chem. Zentr.*, III, 666 (1923); Favorsky and Zalessky-Kibardine, *Bull. soc. chim.*, [4] *37*, 1227 (1925). The dehydration products of this alcohol are being studied exhaustively by C. W. Nash in this Laboratory.

(5) Meerwein, Ann., 419, 121 (1919).

(6) Whitmore and Krueger, unpublished results.

methyls and one butyl, the rearrangement of the butyl still predominated about 2:1. The dehydration of 2,2-dimethylhexanol-1 gave four of the five olefins which would be predicted.' Ozonolysis products of these olefins corresponding to 95% yields were isolated and identified.

The possible courses of the dehydration may be indicated as follows[7]

$(CH_3)_2(C_4H_9)CCH_2OH \longrightarrow (CH_3)_2(C_4H_9)CCH_2 +$ (1)
(1) By shift of butyl $\longrightarrow (CH_3)_2C^+CH_2C_4H_9$ (2)
(1) By shift of methyl $\longrightarrow (CH_3)(C_4H_9)C^+CH_2CH_3$ (3)
(2) By loss of proton from amyl $\longrightarrow (CH_3)_2C{=}CHC_4H_9$ (4)
(2) By loss of proton from methyl $\longrightarrow CH_2{=}C(CH_3)(C_5H_{11})$ (5)
(3) By loss of proton from butyl $\longrightarrow C_3H_7CH{=}C(CH_3)(C_2H_5)$ (6)
(3) By loss of proton from ethyl $\longrightarrow (CH_3)(C_4H_9)C{=}CHCH_3$ (7)
(3) By loss of proton from methyl $\longrightarrow CH_2{=}C(C_2H_5)(C_4H_9)$ (8)

The olefins (4), (5), (6) and (7) were formed as indicated by their ozonolysis products as follows

(4) Acetone and n-valeraldehyde
(5) Methyl *n*-amyl ketone and formaldehyde
(6) Methyl ethyl ketone and n-butyraldehyde
(7) Methyl n-butyl ketone and acetaldehyde

No evidence of ethyl n-butyl ketone could be found. This indicated the absence of (8) among the dehydration products. Olefins (4) and (5) appeared in the ratio 12:1, indicating a predominant loss of hydrogen from the newly formed amyl group as compared with the two methyl groups. In the case of (7) and (6) the ratio was 2:1 in favor of the loss of hydrogen from the newly formed ethyl group as compared with the butyl group. Since the first of these ratios was much higher than similar ratios obtained in dehydrating various alcohols containing methyl and amyl groups,[8] it was decided to dehydrate the tertiary alcohols corresponding to fragments (2) and (3), namely, dimethyl-n-amylcarbinol and methylethyl-*n*-butylcarbinol. The first of these gave olefins (4) and (5) in the ratio 1.4:1 and the second gave olefins (7) and (6) in the ratio 1.6:1 and also a 6% yield of olefin (8) as indicated by the amount of formaldehyde and ethyl n-butyl ketone obtained from the ozonolysis products. The difference between the values of 12:1 and 1.4:1 for the ratios of olefins (4) and (5) formed by dehydration *with* rearrangement of the primary alcohol by means of a small amount of concd. sulfuric acid and by dehydration of the tertiary alcohols by means of a small amount of 50% sulfuric acid is being studied further.

Experimental

Preparation of Dimethyl-*n*-butylcarbinol, its Chloride, and the Corresponding Grignard Reagent.—The carbinol, b. p. 139–142° (740 mm.), 59–61° (25 mm.), n^{20}_{D}

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(7) The hydroxyl is assumed to be removed with its octet leaving the carbon indicated by a + with only a sextet of electrons. By shifts of electron pairs from the adjacent carbon atoms fragments (2) and (3) are obtained.'

(8) Whitmore and Williams, THIS JOURNAL, 55, 406 (1933).

1.4176, was prepared in 8-mole lots from n-butyl Grignard reagent and acetone in 60% yields based on the n-butyl bromide used.[9] The tertiary chloride was prepared by hydrochloric acid in the usual way,[9] b. p. 70–72° (90 mm.), 34–36° (15 mm.), $n_{\rm D}^{20}$ 1.4205.

Dimethyl-n-butylcarbinylmagnesium chloride was prepared in 6-mole lots in 50–60% yields.[10] The details of a typical run follow. A 3-liter flask containing 146 g. of fresh magnesium turnings and a crystal of iodine was heated over a free flame to vaporize the iodine. The flask was stoppered and cooled and then fitted with a reflux condenser, an efficient stirrer and a dropping funnel. Addition of 5 cc. of the pure tertiary chloride and 1 cc. of *n*-butyl bromide started a vigorous reaction. This was maintained by suitable additions of portions of a mixture of 403 g. (3 moles) of the chloride with 500 cc. of dry ether and of a 300-cc. quantity of the same ether. The addition of the chloride solution was mainly at the rate of one drop per second. Vigorous stirring was used throughout the reaction. Then 300 cc. of dry ether was added and finally a more dilute solution of the chloride (403 g. and 1000 cc. of dry ether) was slowly added. The total time of addition of the chloride was sixty-eight hours. The mixture was then stirred for eight hours more, allowed to settle and an aliquot part was titrated with standard acid. Even with the care indicated, nearly half of the tertiary chloride was converted to heptylenes.

Preparation of **2,2-Dimethylhexanol-1.**—Several runs of dimethyl-n-butylcarbinylmagnesium chloride with fornialdehyde, ranging from 0.8 to 3.2 moles, gave yields of the desired alcohol of 41–63%. A typical run follows. During five hours the formaldehyde obtained by heating 100 g. (3.3 moles CH_2O) of paraformaldehyde at 165–170° was carried by a slow stream of dry nitrogen over the surface of a rapidly stirred solution of 3.2 moles of the Grignard reagent in 2100 cc. of ether. The reaction mixture was then stirred and gently refluxed for eight hours. It was decomposed with ice and ammonium chloride in the usual way. The ether layer and extracts were dried with anhydrous sodium sulfate and potassium carbonate overnight, filtered and distilled. After removal of the ether the residue was twice fractionated with a high reflux ratio through a 90 × 2 cm. insulated packed partial condensation column.[11] The final fractions obtained were as follows.

	B. p., °C.	Mm.	G.	$n_{\rm D}^{20}$	
1	36–88	731	17	1.3725	
2	88–90	731	119	1.3940	Heptylenes
3	90–140	731	15	1.4100	
4	54–60	14	45	1.4195	Unchanged chloride
5	60–80	14	12	1.4263	
6	80–82	14	260	1.4304	2,2-Dimethylhexanol-1
7	68–90	2	18	1.4428	
8	Residue		6	1.4609	Brown viscous oil

Dehydration of **2,2-Dimethylhexanol-1.**—Heating the alcohol with 4% of its weight of concd. sulfuric acid for two hours gave only 5% dehydration. Several variations of this experiment and the use of *p*-toluene sulfonic acid also failed to give satisfactory results. Finally a mixture of the alcohol with 6% of its weight of concd. sulfuric acid and 4% of *p*-toluene sulfonic acid, heated for six hours with constant removal by distillation of the products, gave a 70% dehydration with a 63% yield of octylenes. A similar yield was obtained by using 8% by weight of concd. sulfuric acid but slightly more charring took place than when the sulfonic acid was also used. A typical experiment follows. A mixture of 52 g. (0.4 mole) of 2,2-dimethylhexanol-1 and 2.5 cc. of concd. sulfuric acid (sp. gr. 1.84) was added dropwise to a heated 50-cc. Claisen flask with an

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(9) For details see Whitmore and Woodburn, THIS JOURNAL, 55, 361 (1933).

(10) Cf. Whitmore and Badertscher, unpublished results.

(11) Whitmore and Lux, *ibid.*, 54, 3451–3 (1932).

air-jacketed indented side-arm. 30 X 1 cm. The heat was regulated to allow olefins and water to distil over at about 120° as rapidly as they were formed. In one hundred minutes, 57 cc. of oil and 8 cc. of water had distilled. At the end of the process, sulfur dioxide became noticeable and some charred material remained in the flask. The oil layer was washed with water and with dilute sodium bicarbonate solution and dried with anhydrous sodium sulfate. Fractionation through a 70 X 1 cm. indented adiabatic total condensation column using a high reflux ratio[11] gave the following fractions (735 mm.).

	B. p.. °C.	G.	n^{20}_{D}	
1	110–118	0.8	1.4153	Two layers
2	118–120	2.5	1.4167	
3	120–122	28.3	1.4188	Octylenes
4	122–165	2.8	1.4236	
5	165–170	5.8	1.4296	Unchanged alcohol
6	Residue	2.4		Brown viscous oil

Ozonolysis of Heptylenes from **Dimethyl-*n*-butylcarbinyl** Chloride.'*—This olefin mixture, b. p. 88–90° (730 mm.), n^{20}_{D} 1.3946, was obtained as a by-product in the preparation of the chloride because of its partial decomposition during distillation. Since its ozonolysis products probably included both formaldehyde and acetone, it was studied before attacking the more complex mixture of olefins obtained by the dehydration of the alcohols.

Ozonized oxygen was passed for fifteen hours at the rate of 15 liters per hour through a solution of 49 g. (0.5 mole) of the olefin in 300 cc. of 0–35° saturated hydrocarbon13 kept at −10°. Removal of the solvent at room temperature under reduced pressure left 64 g. of colorless liquid ozonide (87% yield). The ozonide was decomposed with zinc and water during about two hours.[12] During the decomposition, 35 cc. of oil was collected. An ether trap at 0° was used to remove organic material from the nitrogen stream used to sweep the products out of the decomposition mixture. This ether was used to extract the water layer of the distillate. The water layer gave qualitative tests for formaldehyde with the fuchsin and resorcinol tests and for acetone by the formation of iodoform and dibenzylidene acetone (m. p. and mixed m. p. 110°). Titration of the water layer with standard base and hydrogen peroxide showed 3.8 g. of formaldehyde and titration with standard iodine solution (for both formaldehyde and acetone) showed 9.0 g. of acetone. The oil layer was fractionated through the 70 X 1 cm. column at 733 mm. with a reflux ratio of about 20:1 to give seven fractions and a residue of 1.9 g. Fractions 1 and 2 had the odors of acetone and butyraldehyde, respectively. Fraction 3, 2.3 g., b. p. 72–75", n^{20}_{D} 1.3861, gave the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde, m. p. 120°, mixed m. p. 119°. Fraction 6, 16.5 g., b. p. 124–128°, n^{20}_{D} 1.3996, gave the semicarbazone of methyl n-butyl ketone, m. p. 116°, mixed m. p. 114°. The isolated ozonolysis products represented yields of 2-methylhexene-1 and -2 of 39 and 31%, respectively, thus indicating a slightly greater tendency for the loss of hydrogen from the two methyl groups than from the one butyl group during the decomposition of the dimethyl-n-butylcarbinyl chloride.

Ozonolysis of the **Olefins** from **2,2-Dimethylhexanol-1**.—The treatment of 56 g. (0.5 mole) of the olefins, b. p. 120–122° (735 mm.), n^{20}_{D} 1.4188, with ozonized oxygen in the usual way gave 70.4 g. of a colorless liquid ozonide (88% yield). Decomposition of the ozonide gave 38 g. of oil. The reflux condenser at 25° allowed acetaldehyde to pass through into an ether solution from which acetaldehyde-ammonia, 1.6 g., m. p. 90°

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(12) For details of technique see Whitmore and Church, THIS JOURNAL, 54, 3712 (1932).

(13) Supplied by the Viking Corporation of Charleston. W. Va.

was formed. The water layer when titrated with standard alkali and hydrogen peroxide and with standard iodine was found to contain 0.45 g. of formaldehyde and 14.6 g. of acetone. The water layer also gave a qualitative test for formaldehyde with resorcinol. The water layer after the titrations gave 2.6 g. of oil on extraction with ether. Thus a total of 56.8 g. of crude products was obtained from the ozonide (89.6% yield). The crude oil, after drying over anhydrous sodium sulfate, was fractionated three times through the 70 × 1 cm. column at 739 mm. to give twelve fractions and a residue of 6 g. Fraction 2, 1.2 g., b. p. 50–60°, n^{20}_{D} 1.3700 gave dibenzylidene acetone, m. p. and mixed m. p. 110°. Fractions 3 and 4, 5.3 g. b. p. 60–75°, n^{20}_{D} 1.379, gave the 2,4 dinitrophenylhydrazone of n-butyraldehyde, m. p. 118 and 119° and mixed m. p. 119 and 120°. Fraction 5, 1.8 g., b. p. 75–80°, n^{20}_{D} 1.380, was identified with difficulty as impure methyl ethyl ketone. Its 2,4-dinitrophenylhydrazone after many crystallizations from absolute alcohol melted at 98° instead of 113°. A mixture with the known 2,4-dinitrophenylhydrazone of methyl ethyl ketone melted at 103° while a mixture with the n-butyraldehyde derivative melted at 85°. It also gave the semicarbazone of methyl ethyl ketone which, after many recrystallizations from 50–70° petroleum ether, melted at 130° instead of 138°. A mixture with the known derivative melted at 133°. Fractions 6 and 7, 0.7 g. and 3.2 g., b. p. 80–98° and 98–103°, n^{20}_{D} 1.3841 and 1.3923, gave the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde, m. p. and mixed m. p. 95°. Fraction 9, 9.7 g., b. p. 123–128°, n^{20}_{D} 1.3999, gave the 2,4-dinitrophenylhydrazone of methyl n-butyl ketone, m. p. 103°, mixed m. p. 105°, and the semicarbazone, m. p. 116°, mixed m. p. 114°. Fraction 11, 2.1 g., b. p. 145–150°, n^{20}_{D} 1.406, gave a semicarbazone which after many crystallizations melted at 101°. A mixture with the semicarbazone of methyl n-amyl ketone melted at 103°. One with the semicarbazone of ethyl n-butyl ketone (m. p. 103°) melted at 78°. The mother liquors from the semicarbazone of the methyl n-amyl ketone gave no indication of the semicarbazone of ethyl n-butyl ketone even after repeated crystallizations. The percentage yields of the carbonyl compounds obtained from the ozonide were as follows: formaldehyde, 3.4; acetaldehyde, 5.9; acetone, 56.9; butyraldehyde, 11 (estimated); methyl ethyl ketone. 11 (estimated); n-valeraldehyde, 10.0; methyl n-butyl ketone, 22.0; methyl n-amyl ketone 4.3. Thus the total isolated yield of ketone products was over 90% while that of the aldehydes was only 30%.

The Dehydration Products of **Methylethyl-*n*-butylcarbinol.**—This carbinol, which corresponds to the rearrangement of a methyl group in 2,2-dimethylhexanol-1, was prepared as follows. n-Butylmagnesium bromide (2.66 moles) was prepared from 415 g. (3 moles) of n-butyl bromide and 75 g. of magnesium in 1000 cc. of dry ether. To this was added during three hours 192 g. (2.66 moles) of redistilled methyl ethyl ketone,[14] b. p. 78–79° (735 mm.), n^{20}_{D} 1.3792. The mixture was decomposed with ice and dilute sulfuric acid and worked up in the usual way. The methylethyl-n-butylcarbinol boiling at 158–159° (731 mm.) and having n^{20}_{D} 1.4238 amounted to 290 g. (83% yield based on the Grignard reagent).

The carbinol was readily dehydrated by refluxing under a 80 × 2 cm. column with 5 cc. of 50% sulfuric acid and removing the water and olefin at the top of the column at a temperature of 115–125°. The product was dried with anhydrous copper sulfate and distilled through the same column.[11] The product, b. p. 119–120° (735 mm.) and n^{20}_{D} 1.4186, weighed 232 g. (93% yield) One mole (112 g) of the olefin product was ozonized in the usual way to give 140 g. of colorless liquid ozonide (87% yield). Decomposition of the ozonide in the usual way gave 93 g. of oil, 3.75 g. of acetaldehyde-ammonia, m. p. 92°, and 1.56 g. of formaldehyde, determined iodimetrically. Ether extraction of the water layer after removal of the formaldehyde and acetaldehyde gave 6.5 g. of oil. Thus

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[14] Supplied by the Shell Development Co. of Emeryville, Calif., through the courtesy of Dr. E. C. Williams.

the total yield of crude products from the ozonide was 82%. Fractionation of the oil through the 70 X 1 cm. column at 732 mm. gave twelve fractions and a residue of 2.1 g. Carbonyl compounds were identified in the various fractions in the usual way by m. p and mixed m. p. determinations of their 2,4-dinitrophenylhydrazones and their semicarbazones. n-Butyraldehyde was found in fractions 1–3, 14.3 g., b. p. 63–74", n_{D}^{20} 1.38. Methyl ethyl ketone was found in fractions 4 and 5, 14.2 g., b. p. 75–78", n_{D}^{20} 1.379 Methyl n-butyl ketone was found in fractions 7 and 8, 25.2 g., b. p. 123–128°, n_{D}^{20} 1.400. Smaller amounts were also found in fractions 6 and 9. Ethyl n-butyl ketone was identified in fractions 10 and 11, 8.6 g., b. p. 143–148°, n_{D}^{20} 1.408. The percentage yields of carbonyl compounds were as follows: formaldehyde, 6.0; acetaldehyde, 7.0; methyl ethyl ketone, 23.0; butyraldehyde, 23.3; methyl *n*-butyl ketone, 38.6; ethyl n-butyl ketone, 4.3. Thus dehydration from the ethyl, butyl and methyl group occurred approximately in the ratio 6: 3: 1.

The Dehydration Products of Dimethyl-*n*-amylcarbinol.—This carbinol, which corresponds to the rearrangement of the butyl group in 2,2-dimethylhexanol-1, was prepared as follows. Methylmagnesium chloride (2.4 moles) in 500 cc. of dry ether was treated with 188 g. (1.3 moles) of ethyl caproate in 800 cc. of dry ether. The crude product was distilled through the 80 X 2 cm. column at 740 mm. A considerable amount of olefin collected at 116–118°. The carbinol boiled at 155–156°, n_{D}^{20} 1.4240. The carbinol was dehydrated with 5 cc. of 50% sulfuric acid in the same way as its isomer. The crude olefin was dried over sodium and distilled, b. p. 117–119° (740 mm.), n_{D}^{20} 1.4138, wt 84 g. (55% yield based on the ethyl caproate). The olefin was ozonized in a 0.4 mole lot in the usual way to give 57.5 g. of ozonide (89% yield). The decomposition of the ozonide gave a 90% yield of crude carbonyl compounds including 1.1 g. of formaldehyde (determined by the hydrogen peroxide method), 10.1 g. of acetone and 44.7 g. of oil. The latter was fractionated at 734 mm. through the 70 X 1 cm. column to give seven fractions and a residue of 4.1 g. The carbonyl compounds were identified in the usual way. Acetone was found in fraction 1, 2.2 g., b. p. 55–60', n_{D}^{20} 1.367; *n*-valeraldehyde in fraction 3, 3.1 g., b. p. 98–103°, n_{D}^{20} 1.392; methyl n-amyl ketone in fraction 5, 15.2 g., b. p. 145–150°, n_{D}^{20} 1.4085. The percentage yields of carbonyl compounds were as follows: formaldehyde. 10.1; acetone, 59.1; n-valeraldehyde, 10.1; methyl n-amyl ketone, 42.1. Thus the dehydration from the one n-amyl and the two methyl groups was about 3: 2.

Summary

1. 2,2-Dimethylhexanol-1 has been dehydrated and the accompanying rearrangements have been determined by ozonolysis of the resulting olefins.
2. The related tertiary alcohols, methylethyl-n-butylcarbinol and dimethyl-n-amylcarbinol, have been dehydrated and their products similarly studied.
3. Certain peculiar relations have been noted in these dehydrations.
4. The heptenes from the decomposition of dimethyl-*n*-butylcarbinyl chloride have been ozonized.

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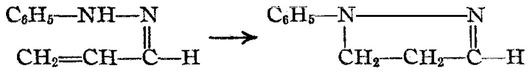
Rearrangement of the Phenylhydrazones of Some Unsymmetrically Substituted Dibenzalacetones[1]

BY L. CHAS. RAIFORD AND JOHN B. ENTRIKIN

Phenylhydrazine and acroleïn[2] interact to give 1-phenylpyrazoline instead of the expected hydrazone. Later work[2] indicated that the



$C_6H_5—NH—N=CH—CH=CH_2 \longrightarrow C_6H_5—N—N=CH—CH_2—CH_2$

(Not isolated)

pyrazoline was formed through the rearrangement of a hydrazone, and that when the latter could be isolated, heating with acetic acid caused rearrangement. The stability of the phenylhydrazones of the type R—CH=CH—CO—R′ depends on the structures of both R and R'. When R is an aryl radical hydroxyl and alkoxyl as substituents in it favor rearrangement, while the nitro radical tends to stabilize the hydrazone. Straus[3] found that the hydrazones obtained from several symmetrically substituted dibenzalacetones rearranged easily when halogen is present in either ketone or hydrazine residue; if present in both, the hydrazone is stable.

Identification of Products.—The methods of distinguishing between these hydrazones and the pyrazolines include the following considerations. The tendency[4] of the first to rearrange to the second is so pronounced that the Knorr[5] color test for pyrazoline bases often shows the presence of the latter in the mother liquors from which the hydrazones were crystallized. Such solutions frequently show also a blue fluorescence if pyrazoline is present. When the product in question can be reduced by sodium amalgam[6] to give aniline, it is regarded as a hydrazone.[7] These are generally rearranged by boiling acetic acid.[8] Products not reduced or rearranged are regarded as pyrazolines. To identify the latter directly Straus[9] found that this product obtained by interaction of phenylhydrazine and dibenzal-

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(1) From the thesis submitted in partial fulfilment of the requirements for the Ph.D. degree at the State University of Iowa.

(2) Auwers and collaborators, *Ber.*, 41, 4230 (1908); 42, 4412 (1909); 54, 1000 (1921).

(3) Straus, *ibid.*, 51, 1458 (1918).

(4) Auwers and Voss, *ibid.*, 42, 4412, 4417 (1909).

(5) Knorr, *Am.*, 238, 200 (1887).

(6) Tafel, *Ber.*, 22, 1854 (1889).

(7) Auwers and Kreuder [*ibid.*, 58, 1983 (1925)] could not reduce the product, m. p. 120–121°, obtained from benzalacetone and *p*-tolylhydrazine. The compound was regarded as a hydrazone because boiling acetic acid changed it to an oil that gave a pronounced violet color when a sulfuric acid solution of it was treated with ferric chloride—a reaction given by pyrazolines generally.

(8) Auwers and Voss [*ibid.*, 42, 4418 (1909)] failed to rearrange the product obtained from cinnamic aldehyde and *p*-nitrophenylhydrazine, although the compound was shown by reduction to be a hydrazone.

(9) Ref. 3, p. 1468.

acetone was oxidized by potassium perrnanganate to give 1,5-diphenylpyrazole-3-carboxylic acid[10] and benzoic acid. He oxidized no product containing acidic substituents and none obtained from unsymmetrical ketones.

In the present work hydrazones were obtained from styryl 4-chlorophenyl and styryl 4-chlorostyryl ketones. In other cases pyrazolines only were isolated. Treatment of the hydrazones with sodium amalgam was unsatisfactory; repeated trials of the first one gave small quantities of aniline; the others gave none. They were rearranged by boiling with acetic acid. To decide which radical of the unsymmetrical ketone was involved in the formation of the pyrazoline and to determine the structure of the latter it was oxidized by the potassium permanganate.

Experimental Part

Styryl 4-Nitrostyryl Ketone.—To a solution of 20 g. of 4-nitrobenzaldehyde in 250 cc. of alcohol, somewhat above room temperature, 20 g. of benzalacetone were added with stirring and the mixture cooled to about 10°. Twenty cc. of 10% sodium hydroxide solution was then added, the stirring continued for two hours, the temperature kept below 18°, and the mixture allowed to stand overnight; yield, 40%. Crystallization from ethyl acetate gave brownish-yellow flakes; m. p. 178–179°.

Anal. Calcd. for $C_{17}H_{13}O_3N$: N, 5.02. Found: N, 4.75.

Other ketones required in this work are on record.

Phenylhydrazone of **Styryl** 4-Chlorophenyl Ketone.—To a solution of 20 g. of the required ketone[11] in 250 cc. of glacial acetic acid, 8.7 g. of phenylhydrazine was added with stirring, and the mixture allowed to stand for twenty-four hours; yield, 46%. Crystallization from alcohol gave yellow needles; m. p. 100–101°.[12] Further crystallization gave a higher melting range, suggesting rearrangement. Boiling this material with acetic acid gave a product that melted at 149–150°, which was regarded as a pyrazoline. The same product was obtained when the original reaction mixture was allowed to stand for five days at room temperature.

Anal.[13] Calcd. for $C_{21}H_{17}N_2Cl$: Cl, 10.67. Found: Cl, 10.36.

The phenylhydrazone of styryl 4-chlorostyryl ketone was obtained in yellow needles that melted at 165–166°; yield, 60%. Recrystallization from acetic acid, acetone, alcohol or ethyl acetate caused partial rearrangement. Boiling it for an hour with acetic acid rearranged it completely to the pyrazoline; m. p. 184–185".

Anal. Calcd. for $C_{23}H_{19}N_2Cl$: Cl, 9.90. Found: Cl, 10.33.

Oxidation of **Pyrazolines.**—In general, 10 g. of pyrazoline was suspended in 200 cc. of water containing 5 g. of sodium carbonate, and this mixture was boiled under a reflux condenser while 40–45 g. of solid permanganate was added in 3 to 4 g. portions as long as the purple color was discharged, usually several hours. The mixture was filtered, the residue digested with sodium hydroxide solution and filtered, and the combined filtrates acidified. The acids liberated were collected and subjected to steam distillation to remove benzoic acid. The non-volatile pyrazole acid was then purified.

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(10) Beyer and Claisen, Ber., **20**, 2186 (1887).

(11) The product used here, made by a standard method, melted at 97°. Dilthey [J. *prakt.* Chem., 101, 199 (1920)] recorded 101°.

(12) Repeated attempts to reduce this material by sodium amalgam gave small quantities of aniline.

(13) Brown and Beal, THIS JOURNAL, **45**, 1291 (1923).

Compounds 2, 3, 4 and 5 (see table) gave small[14] yields of 1.5-diphenylpyrazole-3-carboxylic acid. In all cases except that containing the 3-nitrostyryl radical the required substituted benzoic acid was also isolated in small yield.[15] Table I gives the composition and other properties of the pyrazolines.

TABLE I

PYRAZOLINES FROM UNSYMMETRICAL α,β-UNSATURATED KETONES

Substituted aryl radicals, 1,5-diphenyl-3-	Solvent	Crystal form	Formula	M. p., °C.	Analyses: Halogen, % Calcd.	Halogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
(1) (4-Chlorophenyl)-	Alcohol	Yellow needles	$C_{21}H_{17}N_2Cl$	149–150	10.67	10.71	...	...
(2) (3-Chlorostyryl)-	Ethyl acetate	Dark yellow needles	$C_{23}H_{19}N_2Cl$	153–154	9.90	9.94	...	...
(3) (4-Chlorostyryl)-	Ethyl acetate	Deep yellow needles	$C_{23}H_{19}N_2Cl$	184–185	9.90	10.16	...	...
(4) (3-Nitrostyryl)-	Acetic acid	Orange needles	$C_{23}H_{19}O_2N_3$	182–183	...	...	11.38	11.01[a]
(5) (4-Nitrostyryl)-	Alcohol[b]	Red nodules	$C_{23}H_{19}O_2N_3$	191–192	...	...	11.38	11.30

[a] Done by a modification of Kurschner's method [Z. anal. *Chem.*, 68,209 (1926)].

[b] crystallization from acetic acid gave irregularly shaped crystals that appeared to decompose with frothing at 130–131°, and gave a clear liquid at about 190°, which suggested solvent of crystallization. When heated for twenty-four hours at 135°, 1.9377 g. lost 0.2529 g. Calcd. for $C_{23}H_{19}O_2N_3 \cdot C_2H_4O_2$: $C_2H_4O_2$, 13.99. Found: $C_2H_4O_2$, 13.05. Separate portions of the original material and of the residue left after removal of acetic acid of crystallization, respectively, were crystallized from alcohol. In each case small red crystals that melted at 191–192° were obtained.

Summary and Conclusions

1. Several unsymmetrically substituted dibenzalacetones have been condensed with phenylhydrazine. Hydrazones were isolated in some cases, and in others the products rearranged immediately to the isomeric pyrazolines.

2. In the rearrangement of these hydrazones the closing of the pyrazoline ring involved the unsaturation farthest away from the phenyl nucleus containing the halogen or nitro radical. This was indicated by the fact that in the oxidation of the pyrazolines 1,5-diphenylpyrazole-3-carboxylic acid and benzoic or a substituted benzoic acid were obtained.

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(14) Doubtless due to further oxidation of the pyrazole acid. Oxidation of 1,5-diphenyl-3-styrylpyrazoline, by G. V. Gundy of this Laboratory, gave 39% of the pyrazole acid and 137% of the required benzoic acid. Treatment of a purified sample of pyrazole acid with permanganate gave benzoic acid.

(15) Zimmerman (unpublished work) treated pure bromo- and nitrobenzoic acids with alkaline permanganate and noted destruction of the acids to the extent of 20% or more. When the ketones here used were condensed with *p*-nitro- and *p*-bromophenylhydrazines the initial products had melting points and other properties different from those shown by the compounds obtained by boiling the initial ones with acetic acid. The first were probably hydrazones and the final ones pyrazolines. Oxidation of the latter with permanganate seemed to cause complete degradation. From the product obtained by interaction of 4-bromophenylhydrazine with styryl 3-nitrostyryl ketone, only a small amount of benzoic acid was isolated. The bromide ion was easily detected in the reaction mixture.

3. Oxidation of pyrazolines containing a bromine atom or a nitro radical in the hydrazine residue seemed to cause complete degradation of the molecule. These compounds are still being studied.

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The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. I

BY FRANK C. WHITMORE AND R. J. SOBATZKI[1]

The reaction, $Ar_2Hg + HgX_2 \rightleftharpoons 2ArHgX$, has been the subject of many studies.[2]

The present investigation deals with the influence of inorganic iodides on the reaction. It was suggested by the observation that while sodium iodide in alcoholic solution reverses the reaction in the case of para tolyl compounds, giving a complete conversion to di-p-tolylmercury, it has no effect on phenylmercuric iodide. Early in the investigation cases were found in which the reversibility of the reaction by sodium iodide lay between these extremes. Consequently it became necessary to develop a method for analyzing mixtures of Ar_2Hg and ArHgI. This was accomplished satisfactorily by iodimetry.[3] The method can best be illustrated by the two equations

$$ArHgI + I_2 \longrightarrow ArI + HgI_2$$
$$Ar_2Hg + 2I_2 \longrightarrow 2ArI + HgI_2$$

Thus a given amount of mercury in a diarylmercury will react with twice as much iodine as the same amount of mercury in an arylmercuric iodide. The method was found to give satisfactory results with known mixtures of arylmercuric halides and diarylmercury compounds.

The following arylmercuric iodides were converted to the mercury diaryls by refluxing with an excess of alcoholic sodium iodide: o-tolyl, m-tolyl, *p*-tolyl, m-xylyl, mesitylyl, α-naphthyl and β-naphthyl. Phenylmercuric iodide showed no change even after refluxing for three hundred hours with alcoholic sodium iodide. Benzyl- and cyclohexylmercuric iodides decomposed on long heating with sodium iodide. *p*-Ethylphenyl-

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[1] Research Fellow of the Public Health Institute of Chicago. This paper is abstracted from a thesis submitted in partial fulfilment of the requirements for the Ph.D. degree at Northwestern University.

[2] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, pp. 69–67; Whitmore, THIS JOURNAL, **41**, 1841 (1919); Hein and Wagler, *Ber.*, **58B**, 1499 (1925); Jurgens, Rec. *trav.* chim., **45**, 61 (1926); Whitmore, Hanson and Carnahan, THIS JOURNAL, **51**, 894 (1929).

[3] This method was developed at Northwestern University by Messrs. Louis Ehrenfeld and R. J. Sobatzki independently, the former for analyzing mixtures of C–Hg and O–Hg compounds and the latter for analyzing mixtures of C–Hg and C–Hg–C compounds.

mercuric iodide gave a mixture of unchanged material and di-*p*-ethylphenylmercury in which the two substances could be distinguished by their characteristic crystalline forms. When *p*-cymylmercuric chloride was refluxed with excess of alcoholic sodium iodide, crystals of the pure di-p-cymylmercury separated on cooling. This was proved by analysis and by reaction with mercuric chloride to give a quantitative yield of pure p-cymylmercuric chloride. A careful study of this reaction showed the existence of a very sensitive equilibrium. When the mixture of sodium iodide and *p*-cymylmercuric chloride was heated with alcohol a yellow solution was formed at once. When this solution was cooled crystals of di-*p*-cymylmercury separated at once. In an effort to find whether the diarylmercury existed in the hot solution, the latter was poured into a large volume of ice water. The solid which precipitated was found to be *p*-cymylmercuric iodide contaminated by about 1% of the diarylmercury compound. These results showed that the hot solution contained the following system in equilibrium.

$$2C_{10}H_{13}HgI + 2NaI \rightleftharpoons Na_2HgI_4 + (C_{10}H_{13})_2Hg$$

It thus became necessary to study conditions which might influence such an equilibrium. The relative solubilities of a number of arylmercuric iodides and the corresponding diarylmercury compounds in alcohol at 25° were determined. In some cases the diarylmercury was more soluble and in others the arylmercuric iodide was more soluble, but the difference in solubilities of corresponding compounds was not more than five-fold except in the case of the phenyl compounds in which case the diarylmercury was forty times as soluble as the arylmercuric iodide. This peculiarity explains the impossibility of converting phenylmercuric iodide to diphenylmercury by means of sodium iodide. It is not possible to get a sufficient concentration of sodium iodide in alcohol to overcome the effect of the unfavorable solubility ratio. In the case of the *p*-tolyl compounds in which the formation of di-*p*-tolylmercury is so readily caused by sodium iodide, the solubility of *p*-tolylmercuric iodide is almost five times as great as that of di-p-tolylmercury.

The effect of the relative concentration of sodium iodide on a number of these reactions was studied. In each case the mixture was refluxed and then cooled. In the case of p-ethylphenylmercuric chloride a molar ratio of sodium iodide to ArHgCl of 3.5:1 gave a mixture containing 11% of the diarylmercury; a ratio of 4.5:1 gave 64% and a ratio of 9:1 gave complete conversion to di-p-ethylphenylmercury.

The effect of relative concentration on the reversibility of the reaction was likewise studied. A molar ratio of Na_2HgI_4 to di-*p*-ethylphenylmercury of 1:1 gave a 97% conversion to *p*-ethylphenylmercuric iodide, while molar ratios of 2:1, 4:1 and 8:1 gave conversions of 98, 99 and 99.8%, respectively.

By using a molar ratio of sodium iodide to benzylmercuric chloride of 10:1 it was possible to obtain a complete conversion to dibenzylmercury.

In the case of m-tolylmercuric chloride, a molar ratio of sodium iodide of 3.5:1 gave an impure product containing only **30%** di-m-tolylmercury, while a molar ratio of 8:1 gave the pure diarylmercury. In the case of o-tolylmercuric chloride a molar ratio of sodium iodide of 4.5:1 was sufficient to form di-o-tolylmercury. With phenylmercuric chloride a molar ratio of sodium iodide of 16:1 failed to give any diphenylmercury.

The influence of the volume of alcohol and of the time of refluxing was studied with the *p*-tolylmercuric compounds. A moderate volume was found to be as effective as a large volume. The time of refluxing was reduced to an approximate limit of ten minutes without cutting down the yield of diarylmercury.[4]

A number of mixtures of arylmercuric iodides and sodium iodide in various molar ratios were brought to equilibrium in boiling alcohol and then poured into large volumes of cold water. Analyses of the precipitated products by iodimetry showed them to consist almost entirely of arylmercuric iodides. This was in spite of the fact that the same solutions on cooling gave the diarylmercury compounds, with the single exception of the phenylmercuric compounds.

Experimental

Preparation of the Mercury Compounds.—These were made by known reactions. The results are summarized in Table I.

TABLE I

Compound	Method	Yield, %	Melting point, °C.		Analysis, Hg	
			Obs.	Lit.	Calcd.	Found[a]
Phenyl-HgI	*e*	66	265–266	266		
Diphenyl-Hg	*d*		120	122–123		
o-Tolyl-HgCl	*c*	42	145–146	146		
o-Tolyl-HgBr	*e*		169.5		53.98	54.0
o-Tolyl-HgI	*e*		176		47.93	48.0
Di-o-tolyl-Hg	*h*		106.5–107	107		
m-Tolyl-HgCl	*c*	27[f]	159.5–160	160		
m-Tolyl-HgI	*e*		161	162		
Di-m-tolyl-Hg	*h*		101–102	102		
p-Tolyl-HgCl	*c*	51	233	233		
p-Tolyl-HgI	*e*	90	220	220		
Di-p-tolyl-Hg	*h*		237	238		
Benzyl-HgCl	*g*		103–104	104		
Benzyl-HgI	*i*		117	117		
Dibenzyl-Hg	*d*		110	111		
p-Ethylphenyl-HgCl	*c*	65[j]	221		58.82	58.8
p-Ethylphenyl-HgBr	*e*		227–228		52.02	51.9
p-Ethylphenyl-HgI	*e*		229		46.38	46.3
Di-*p*-ethylphenyl-Hg	*h, d*		136.5		48.86	48.8

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(4) Contrast the long refluxing recommended in "Organic Syntheses," 1923, Vol. III, p. 65.

TABLE I *(Concluded)*

Compound	Method	Yield, %	Melting point, °C. Obs.	Melting point, °C. Lit.	Analysis, Hg Calcd.	Analysis, Hg Found"
Phenylethyl-HgBr	*g*	65	173 dec.	169k		
Phenylethyl-HgI	*h*		154		46.38	46.3
Mesityl-HgCl	*l*		199–200	200		
Dimesityl-Hg	h		230	236		
p-Cymyl-HgCl	*c*	62j	155	156		
p-Cymyl-HgI	e		169	169		
Di-p-cymyl-Hg	*h*		134	134		
Cyclohexyl-HgBr	*g*		152-153	153		
Cyclohexyl-HgI	*m*		143	143		
or-Naphthyl-HgC1	*c*		187–188	188–189		
Di-or-naphthyl-Hg	*h*		240–241	243		
β-Naphthyl-HgCl	*c*		268–270	271		
Di-*β*-naphthyl-Hg	*h*		237–238	247–248b		

[a] Analyses are given only for new compounds although they were performed on most of the known compounds as well. The figures given are the average of at least two analyses.

[b] Beattie and Whitmore, unpublished results.

[c] Sulfinic acid method of Peters, *Ber*., 38, 2567 (1905), as modified in "Organic Syntheses," 1923, Vol. III, p. 99.

[d] Copper and pyridine method of Hein and Wagler, *Ber*., 58B, 1499 (1925).

[e] Action of the R_2Hg compound with HgX_2 in boiling alcohol.

[f] Yield based on the m-toluidine used in making toluene-*m*-sulfinic acid.

[g] Action of the RMgX compound with an excess of HgX_2.

[h] Action of RHgCl with excess of sodium iodide in boiling alcohol. By increasing the ratio of NaI:RHgCl, the time of refluxing could be decreased greatly; cf. "Organic Syntheses," 1923, Vol. III, p. 65.

[i] Action of RHgCl with 1 mole of potassium iodide or sodium iodide.

[j] Yield based on the sulfonyl chloride used to make the sodium sulfinate.

[k] Hill, THIS JOURNAL, 50, 167 (1928).

[l] Direct mercuration with mercuric acetate.

[m] Obtained from cyclohexylmercuric bromide even with 5 moles of sodium iodide.

Determination of C-Hg Linkage by Iodimetry.—About 0.1 g. of mercuri-bis compound or 0.2 g. of organomercuric halide, weighed accurately, is mixed with 1 g. of potassium iodide, 2 cc. of chloroform, 25 cc. of water and 25.00 cc. of approximately 0.1 *N* iodine solution in a 100-cc. Erlenmeyer flask attached to a reflux condenser by a ground joint. The flask is heated enough to cause the chloroform to reflux gently for fifteen to thirty minutes. During the refluxing 25.00 cc. of the iodine solution used is titrated

TABLE II

SOLUBILITIES OF ARHGI AND AR$_2$HG

Ar	G. per 25 cc. of soln. in 95% alcohol at 25° Ar_2Hg	G. per 25 cc. of soln. in 95% alcohol at 25° ArHgI	Moles per liter of solution Ar_2Hg	Moles per liter of solution ArHgI	Ratio of molar solubilities Ar_2Hg:ArHgI
Phenyl	0.359	0.009	0.0405	0.0010	40:1
m-Tolyl	.1862	.0616	.0149	.00588	2.5:1
p-Tolyl	.008	.042	.00083	.0040	1:4.8
p-Ethylphenyl	.0949	.0509	.00924	.00488	1.9:1
Benzyl	.040	.104	.0041	.0109	1:2.7
2-*p*-Cymyl	.020	.051	.0018	.0044	1:2.4

TABLE III

$ArHgX + NaI \longrightarrow Ar_2Hg$

Ar	X	ArHgX (g)	Molar ratio NaI: ArHgX	Vol. 95% alcohol, cc.	Refluxing time	Product	M. p., °C.	Known m. p., °C. Ar₂Hg	Known m. p., °C. ArHgI	Crude crystals Hg (C-Hg basis) Found av.	Crude crystals Hg (C-Hg basis) Calcd. Ar₂Hg	Crude crystals Hg (C-Hg basis) Calcd. ArHgI
Phenyl	Iodide	9.0	5.5:1[a]	300	300 hrs.	ArHgI	265–266	121–123	266			
Phenyl	Iodide	1.0	16:1	100	3 hrs.	ArHgI	265					
o-Tolyl	Iodide	0.5	4.4:1	50[b]	15 min.	Mixture				99.6	104.9	47.9
		0.5	9:1	30[c]	15 min.	Ar_2Hg				103.1		
m-Tolyl	Chloride	6.0	3.6:1	200	27 hrs.	Mixture	92–94	102	162	64.9	104.9	47.9
	Iodide	2.0	9:1	125	15 min.	Ar_2Hg	101–102			104.9		
p-Tolyl	Chloride	0.50	3.5:1	25	1 hr.	Ar_2Hg[d]	235–237	238	220	105.6[e]	104.9	47.9
	Chloride	0.50	3.5:1	25	2 hrs.	Ar_2Hg[d]	232–236			104.9		
					17 hrs.		228–236			105.3		
					15 min.					103.2		
					10 min.					104.0		
					5 min.					101.7		
				10	15 min.					93.0		
				10	10 min.					102.8		
				10	4 min.					93.1		
				10	10 min.[f]					101.4		
				10	5 min.[f]					88.3		
Benzyl	Chloride	5.0	4:1	200	10 min.	Mixture	88	111	117	67.3	104.9	47.9
		2.0	4.5:1	160	15 min.	Mixture	89–91			74.3		
		1.6	11:1	60	10 min.	R_2Hg	110–111			103.1		
p-Ethylphenyl	Chloride	10	3.5:1	250	20 hrs.	Mixture	129	136.5	229	75.1	97.7	46.4
		0.5	4.5:1	40	5 min.[g]	Mixture				89.7		
		0.5	9:1	60	5 min.	R_2Hg	136			98.1		
		0.5	9:1	60	5 min.[h]	R_2Hg	136.5			97.7		
Phenylethyl	Bromide	5.0	5:1	200	20 min.	RHgI	154	Unstable	154	46.6	97.7	46.4
		1.0	23:1	50	1 hr.	RHgI				46.9		
		1.0	23:1	50	72 hrs.	Decomp. and RHgI				46.8		
2-*p*-Cymyl	Cl	10.0	3.7:1	200	7 hrs.	R_2Hg	133.5	134				
?-*m*-Xylyl	Cl	4.0	4.5:1	200	17 hrs.	R_2Hg	140–147[i]		169	96.9	97.7	46.4
Mesitylyl	Cl	1.5	4.5:1	100	24 hrs.	R_2Hg	230	236	178	90.3	91.5	44.9
Cyclohexyl	Br	2.0	4.9:1	150	30 min.	RHgI	143	78.9	143			
	Iodide	2.0	4.9:1	150	60 hrs.	No C–Hg cpd. Metallic Hg						
α-Naphthyl	Cl	5.0	4.8:1	250	13 hrs.	R_2Hg	240	243	185	87.9	88.3	44.1
β-Naphthyl	Cl	1.0	4.9:1	250	19 hrs.	R_2Hg	237	238	251	87.8	88.3	44.1

[a] Potassium iodide used. [b] After refluxing the solution was evaporated to 10 cc. and allowed to crystallize at 20°. [c] Evaporated to 10 cc. and crystallized at 10°. [d] The yields of R_2Hg obtained in the *p*-tolyl experiments averaged 86%. [e] In the *p*-tolyl series a small amount of finely divided mercury was observed. This may account for the high results in the mercury determination. [f] Vigorous mechanical agitation during refluxing. [g] Crystallized at 5°. [h] Crystallized at 0°. [i] Repeated crystallization failed to separate the isomers which were present.

TABLE IV

$Ar_2Hg + Na_2HgI_4 + NaI \longrightarrow ArHgI$

Ar	G. Ar_2Hg	Molar ratio Na_2HgI_4: Ar_2Hg	Molar ratio excess NaI: Ar_2Hg	Alcohol, 95% used, cc.	Product	M. p., °C.	Known m. p., °C. Ar_2Hg	Known m. p., °C. ArHgI	Hg(C-HgCl) Found Average	Hg(C-HgCl) Calcd. Ar_2Hg	Hg(C-HgCl) Calcd. ArHgI
Phenyl	0.885	1:1	18:1	100	RHgI	263–264	123	266			
Phenyl	1.06	1:1	3:1	75	RHgI[a]	265–266					
Benzyl	0.040	1:1	0	25	Mixture[b]						
p-Ethylphenyl	.205	1:1	0	30					48.2	97.7	46.4
	.205	2:1	0	30					47.3		
	.41	4:1	0	25	RHgI	228–228.5	136.5	229	46.9		
	.41	8:1	0	25	RHgI	228.5–229		229	46.5		
2-*p*-cymyl	.196	1:1	1:1	50	R_2Hg	133–134	134	169			

[a] 94% yield. [b] This experiment was not repeated because of lack of material.

TABLE V

DATA ON FROZEN EQUILIBRIUM MIXTURES IN BOILING ALCOHOL WITH VARYING AMOUNTS OF IODIDES IN SOLUTION

Ar	Molar ratio NaI:ArHg	Hg. (C-Hg basis calcd. for) Found average	Hg. (C-Hg basis calcd. for) Ar_2Hg	Hg. (C-Hg basis calcd. for) ArHgI	Molar ratio ArHgI:Ar_2Hg at equilibrium	Ratio of molar solubilities at 25° ArHgI:Ar_2Hg
Phenyl	16:1	50.5	113.1	49.6	50:1	1:40
p-Tolyl	4:1	49.2	104.9	47.9	40:1	5:1
	12:1				20:1	
Benzyl	34:1	53.4	104.9	47.9	10:1	2:1
p-Ethylphenyl	12:1	46.7	97.8	46.4	150:1	1:2
p-Cymyl	4:1	44.0	86.0	43.6	70:1	2:1

with accurately standardized sodium thiosulfate solution (approximately 0.05 *N*). The flask containing the reaction mixture is cooled, acidified with 2 drops of concd. hydrochloric acid and titrated with the standard thiosulfate. The difference in the thiosulfate used here and with the blank iodine titration gives a measure of the C–Hg linkage present, each such linkage corresponding to two equivalents of iodine or thiosulfate.

Before the method was applied in the research it was tried on several pure substances and known mixtures. Of these only three examples will be given. (a) A sample of 0.1593 g. of o-tolylmercuric bromide was refluxed for thirty minutes with 25.00 cc. of the iodine solution. The titration of the 25.00-cc. blank of the iodine solution required 24.80 cc. of 0.05578 N sodium thiosulfate solution. The unreacted iodine in the refluxed mixture required 9.38 cc. of the same thiosulfate solution for its titration. Thus the C–Hg bonds in the mercury compound reacted with iodine equivalent to 15.42 cc. of the 0.05578 N solution which, in turn, is equivalent to 54.06% of mercury (as C–Hg) in the o-tolylmercuric bromide. The calculated percentage is 53.98. If the compound analyzed had contained the C–Hg–C combination the percentage found on the C–Hg basis would have been divided by two to get the actual percentage of mercury in the compound. Thus diphenylmercury which contains 56.57% mercury would show 113.1% mercury on the C–Hg basis when determined by iodimetry. (b) A mixture was made up of 0.0423 g. of *p*-ethylphenylmercuric chloride and 0.0298 g. of di-*p*-ethylphenylmercury. This reacted with iodine equivalent to 10.90 cc. of 0.04956 *N* thiosulfate indicating 75.02% mercury (C–Hg basis). The calculated amount for the mixture is 74.9% (C–Hg basis). (c) A similar experiment using 0.0288 g. of the ArHgCl and 0.0453 g. of the Ar_2Hg compounds required iodine equivalent to 12.30 cc. of the 0.04956 N thiosulfate, indicating 82.47% mercury (C–Hg basis) as compared with the calculated value of 82.59% for this mixture.

Solubility of the Mercury Compounds in Alcohol.—After several more complicated methods for determining the concentration of the saturated solutions were tried, the following simple procedure was adopted. A saturated solution of the mercury compound in alcohol at 60–70° was prepared. The solution and excess of solid were then stirred and cooled to 25° and kept at that temperature in a thermostat for seventy-two hours. Several 25-cc. samples were removed by means of a filter pipet and transferred to weighed beakers. The main portion of the alcohol was removed at 60–70° in an air-bath (hood). When the residual volume was 5 cc. the beakers were transferred to vacuum desiccators and dried to constant weight. The accuracy of the method was determined by dissolving in alcohol weighed amounts of a variety of arylmercuric halides and diarylmercury compounds and recovering them. In each case the weight of material after the experiment was from 0.5 to 1 mg. greater than that introduced. Thus the method was sufficiently accurate for our purposes. The results are given in Table II.

Action of Alkali Iodides with the Arylmercuric Halides.—The results of the action of varied amounts of sodium and potassium iodides in refluxing alcoholic solution with the various arylmercuric halides are given in Table III.

Action of Diarylmercury Compounds with the Complex Alkali Mercury Iodides.—The experiment with diphenylmercury is typical. A mixture of 2.25 g. (5 mols) of sodium iodide, 1.36 g. (1 mol) of mercuric iodide and 1.06 g. (1 mol) of diphenylmercury in 75 cc. of alcohol was refluxed for thirty minutes. The hot solution had the characteristic yellow color of Na_2HgI_4 solutions. On cooling, this color disappeared and platelets of phenylmercuric iodide separated; m. p. 255–256°, yield 2.42 g. or 94%.

The results of similar experiments with other mercury compounds are given in Table IV.

The Ratio of Concentrations of the Arylmercuric Iodides and the Diarylmercury Compounds in Equilibrium Mixtures in Alcohol at the Boiling Point.—The mixture of a mercury compound which had been refluxed with a known ratio of sodium iodide was poured into a large volume of cold water to precipitate all the mercury compounds present. Thus the equilibrium was essentially "frozen." The precipitate was analyzed and the ratio of $ArHgI:Ar_2Hg$ calculated. The results appear in Table V.

Failure to Produce Diphenylmercury by Means of Iodides.—A solution of 9 g. (1 mol) of phenylmercuric iodide and 20.0 g. (5.5 mols) of potassium iodide in 300 cc. of 95% alcohol was refluxed for three hundred hours. The mixture was cooled. The crystals which separated were washed and dried, m. p. 265–266". The mother liquor was gradually evaporated to yield five crystalline fractions. The first four showed the same m. p. 265°. The last fraction, obtained by evaporating the final mother liquor to dryness, washing with alcohol and water and drying, melted at 264–265°. The m. p. of phenylmercuric iodide is 266° and that of mercury diphenyl is 120". Thus none of the latter substance was formed. A similar experiment using sodium iodide gave the same result.

Action of Mercury Diphenyl with Cold Solutions of Mercuric Salts.—The conversion of mercuri-bis compounds to organomercuric halides is usually carried out by refluxing the former with mercuric halides in alcohol or acetone solution. In the phenyl series this vigorous treatment was found to be unnecessary. Thus the mixing of cold solutions of 0.355 g. of diphenylmercury in 50 cc. of alcohol and 0.272 g. of mercuric chloride in 20 cc. of alcohol gave an *immediate* precipitate of phenylmercuric chloride, m. p. 250–251°. The filtrate gave no test for mercuric ions with bases.

Similarly cold solutions of 0.177 g. of diphenylmercury in 20 cc. of alcohol and 0.227 g. of mercuric iodide in 40 cc. of alcohol gave an immediate precipitate of phenylmercuric iodide, m. p. 265–266°.

The tendency to the formation of ArHgX is apparently not limited to cases in which that product precipitates from the reaction mixture. Thus cold solutions of 0.048 g. of di-*p*-tolylmercury in 200 cc. of alcohol and 0.057 g. of mercuric iodide in 20 cc. of alcohol gave no precipitate on mixing but the resulting solution gave no precipitate with sodium hydroxide, showing that the mercuric iodide had reacted with the diarylmercury.

A similar experiment with cold alcoholic solutions of di-*p*-ethylphenylmercury and mercuric chloride gave a precipitate of *p*-ethylphenylmercuric chloride, m. p. 221°, yield 94%.

Summary

1. The relation of arylmercuric halides to diarylmercury compounds has been studied from the point of view of the equilibrium

$$2ArHgX \rightleftharpoons Ar_2Hg + HgX_2$$

2. The alkali iodide method for forcing this reaction to the right has been studied with thirteen arylmercuric iodides. With ten of these it was successful.

3. A new method for mercury analysis of organic mercury compounds has been developed. This is particularly useful in determining the proportions of R_2Hg and $RHgX$ in a mixture of the two. It is also valuable in determining the amount of organic mercury compound in the presence of inorganic mercury compounds.

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The Hydrolysis and Rearrangement of Certain Olefin Dibromides Containing a Tertiary Bromine

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This rearrangement was discovered by Eltekow who heated isobutylene dibromide with twenty volumes of water and obtained isobutyraldehyde.[1] Later using lead oxide Ipatiew hydrolyzed the dibromide from tertiary amyl alcohol and bromine and obtained methyl isopropyl ketone and methylethylacetaldehyde.[2] Later Froebe and Hochstetter studied the formation of ketones by the hydrolysis of dihalides.[3] The preparation of the dibromides from tertiary alcohols and bromine has been studied by many workers.[2,4]

In this Laboratory it was found that the use of high temperatures and pressures or of lead oxide is unnecessary in the hydrolysis of the dibromide of isobutylene and of trimethylethylene. The products isobutyraldehyde and methyl isopropyl ketone could be distilled out as formed by the use of an effective column. This method was used for converting tertiary amyl alcohol to the large amounts of methyl isopropyl ketone needed in some rearrangement studies.[5] In view of the success with the two lower members of this series of dibromides repeated attempts have been made during several years to extend this reaction to higher tertiary alcohols as a general means of preparing ketones of the type, RR'CHCOR". Of thirteen tertiary alcohols or related dibromides containing more than five carbons, which were studied, only four gave identifiable products. The others gave mainly tars. In a few cases indications of the formation of conjugated dienes and of allenes were obtained. 2,3-Dibromo-2-methylpentane gave a 25% yield of 2-methylpentanone-3; 2,3-dibromo-3-methylpentane gave a 20% yield of 3-methylpentanone-2; 2,3-dibromo-3-ethylpentane gave a small yield of 3-ethylpentanone-2; and 2,3-dibromo-2-methylhexane gave a 33% yield of 2-methylhexanone-3. The most complex dibromides studied were 1,2-dibromo-2,3,3-trimethylbutane and 2,3-dibromo-2-methyltridecane.

Both the positive and negative results obtained are interesting from the point of view of rearrangements.[6] In the two cases which give good yields,

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(1) Eltekow, *J. Russ. Phys.-Chem. Soc.*, 10,215 (1878); *Chem. Zentr.*, 516 (1878); cf. Krassuski, *ibid.*. *I*, 628 (1902).

(2) Ipatiew, *J. prakt. Chem.*, [2] 53, 266 (1896).

(3) Froebe and Hochstetter, *Monatsh.*, 23, 1076 (1902).

(4) Étard, *Compt. rend.*, 114, 755 (1892); Albizky, *J. Russ. Phys.-Chem. Soc.*, 69, *304* (1897); Henry, *Bull. acad. roy. Belg.*, 1906, 424; *Rec. trav. chim.*, 26, 116 (1907); Mereschkowski, *J. Russ. Phys.-Chem. Soc.*, 46, 1940 (1913).

(5) Whitmore and Evers, THIS JOURNAL, 66, 812 (1933).

(6) *Cf.* Whitmore, *ibid.*, 6 4 3274 (1932).

the removal of the tertiary bromine with its complete octet of electrons leaves the fragments

$$(CH_3)_2C^+—CH_2Br \text{ and } (CH_3)_2C^+—CHBr—CH_3$$

These unstable systems might undergo a shift of an electron pair with its attached atom or group or the loss of a proton to give unsaturated compounds. The tendency for the latter in the case of methyl groups is small.[7] The shift of an electron pair with a proton would give the following

$$(CH_3)_2CH—C^+HBr \text{ and } (CH_3)_2CHC^+Br—CH_3$$

which would hydrolyze at once to give isobutyraldehyde and methyl isopropyl ketone. When larger groups than methyl are involved, the tendency to lose protons to give olefins and diolefins increases. These would tend to polymerize in the presence of the acid formed in the hydrolysis.

Experimental

1,2-Dibromo-2-methylpropane.—Preliminary experiments indicated that tertiary butyl alcohol and bromine do not react appreciably at 20' but that near the boiling point of the alcohol a rapid reaction occurs with the production of a colorless dibromide boiling mainly at 140–150°. It was finally found best to keep the alcohol at 60–70° and to add the bromine with stirring at such a rate that no unreacted bromine accumulated and the temperature did not rise. The product consisted of two layers. The upper layer contained water and hydrobromic acid. In six runs involving a total of 1.4 kg. of tertiary butyl alcohol and 3.1 kg. of bromine the yield of dibromide, b. p. 143–150' (735 mm.). was 68–75%. From 10 to 16% of the bromine appeared as hydrobromic acid. Considerable amounts of polybromides and smaller amounts of tertiary butyl bromide were also formed.

The isobutylene dibromide was hydrolyzed in 2-mole lots by heating with 2 liters of water in a flask equipped with a 90 × 1.5 cm. packed column. At first heat was applied to give refluxing without any distillation. Later the heat was increased to distil off the isobutyraldehyde as formed (59–64' at top of column). After fifty hours the dibromide layer had disappeared and 185 g. of crude product had distilled. This was treated with hydroquinone and distilled through an efficient 45 × 1 cm. column to give 108 g. of isobutyraldehyde, b. p. 58–65' (740 mm.), a yield of 75%. The time of hydrolysis and distillation for a one-mole run of the dibromide was cut from fourteen to three hours by the use of an efficient stirrer.

It was found possible to make isobutyraldehyde directly from the crude bromination mixture from tertiary butyl alcohol in 50–55% yields. Distillation of the water layer gave about 80% of the bromine as constant boiling hydrobromic acid.

2,3-Dichloro-2-methylbutane, b. p. 134–138° (735 mm.), refluxed with water and with disodium phosphate solution for thirty hours gave only 10% hydrolysis. Refluxing with 1 mole of sodium hydroxide solution for twenty-four hours gave 17% hydrolysis. Methyl isopropyl ketone was identified.

1,2-Dibromo-2-methylbutane.—Secondary butylcarbinol,[8] b. p. 125–127.5° (735 mm), was treated with constant boiling hydrobromic acid and sulfuric acid to give a 40% yield of 1-bromo-2-methylbutane, b. p. 117–118.4° (732 mm.). A considerable amount of tertiary amyl bromide was also formed. Attempts to convert the 1-bromo

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(7) Cf. Whitmore and Woodburn, THIS JOURNAL, 66, 361 (1933): Wbitmore and Williams, *ibid.*, 55, 406 (1933).

(8) Supplied by the Sharples Solvents Corp. of Philadelphia.

TABLE I

Carbinol	G.	Dbromide	G.	Yield %	B. p., °C.	Mm.	n_{D}^{20}	Hydrolysis product identified	B. p., °C.	Mm.	n_{D}^{20}	Yield, %
Dimethyl-propyl-[a]	204	2,3-Dibromo-2-methylpentane	313	64	66–68	15	1.4975	Ethyl isopropyl ketone (semicarbazone m. p. 93.5–94°)[b]	111–115	...	1.4000	25[c]
Dimethyl-butyl-[a]	232	2,3-Dibromo-2-methylhexane	337	71	75–78	6	1.5024[e]	Propyl isopropyl ketone (semicarbazone[d] m. p. 118–118.5°)	130–133	738	1.4086	33
Dimethyl-undecyl-	75	2,3-Dibromo-2-methyltridecane	118[g]					Partial hydrolysis. No product[u]				
Dimethyl-isobutyl-[f]	59	2,3-Dibromo-2,4-dimethylpentane	117[g]					Charred, tar[h]				
Methyl-di-ethyl-[i]	102	2,3-Dibromo-3-methylpentane[j]	122	50	48–50	5	1.5085	Methyl *sec.*-butyl ketone (semicarbazone m. p. 94-95°)[k]	114–117	732	1.4010	20
					72–74	15						
Methylethyl-butyl-	65	Much charring	11		56–64	4						
Triethyl-[l]	125	2,3-Dibromo-3-ethylpentane	190	63	73–77	4	1.5098[m]	3-Ethylpentadiene-1,3[n]	97–99	735	1.4508	30
								3-Ethylpentanone-2 (semicarbazone m. p. 93-94°)[o]	132–135	734	1.4140	10
Methylethyl-isopropyl[a]	232	2,3-Dibromo-2,3-dimethyl-pentane[t]	133	51	60–85	10	1.496	Methyl tertiary amyl ketone (semicarbazone m. p. 135.5–137°)[s]	129–130.5	733	1.4150	10
Methyl-di-butyl-	79	4,5-Dibromo-5-methylnonane	52	34	100–107	2.2		Partial hydrolysis. No product[u]				
Methylbutyl-isopropyl-[a]		2,3-Dibromo-2,3-dimethylheptane[q]						Unsaturated[p]	45–52	25		
Methylamyl-isopropyl-[a]	15	2,3-dibromo-2,3-dimethyloctane[r]	36[g]					None[u]				
Dimethyl-*tert.*-butyl-		1,2-Dibromo-2,3,3-trimethyl-butane[q]						Trace of aldehyde[u]				

[a] For the preparation of these carbinols see Whitmore and Evers, Tars JOURNAL, 55,812 (1933).

[b] Fournier, *Bull. soc. chim.*, [4] 7, 840 (1910), gives m. p. 95°.

[c] The high boiling fractions gave indications of a bromohydrin with strong lachrymatory properties.

[d] Meerwein, *Ann.*, 419, 140 (1919), gives m. p. 119°.

[e] n_D^{18} 1.5035; n_D^{19} 1.5029; d_4^{25} 1.5184.

[f] To prevent chamng, it was necessary to brominate this carbinol at 0°. It required 103 hrs.

[g] The crude dibromide was not distilled.

[h] The only volatile products were 6 g., b. p. 83–101°, and 9 g., b. p. 101–127°. These contained bromine.

[i] Prepared in 60% yield by the action of ethylmagnesium bromide with ethyl acetate, b. p. 40–43° (25 mm.), n_D^{20} 1.4168. Pariselle and Simon, *Compt. rend.*, 173, *86* (1922), give b. p. 121°, n_D^{20} 1.418.

[j] Bromination in carbon tetrachloride solution at 65–75°.

[k] Zelinsky, *Ber.*, 34,2865 (1901), gives the b p. of the ketone as 118" (760 mm.) and its n_D^{18} as 1.4002; Courtot, *Bull. soc. chim.*, [3] 35,981 (1906), gives the m. p. of the semicarbazone as 95–96".

[l] Prepared in 79% yield from diethyl carbonate and ethylmagnesium bromide [Moyer and Marvel, "Organic Syntheses," 1931, Vol. XI, p. 99], b. p. 136–139.5" (740 mm.), 52° (17 mm.), n_D^{20} 1.4290.

[m] n_D^{15} 1.5120.

[n] Carbon and hydrogen and molecular weight determinations indicated the formula C_7H_{12}. Heating with sodium gave no acetylene derivative such as would be expected from an allene. On standing in a closed bottle for three months it changed to a viscous polymer which only partly distilled at 260°.

[o] Tiffeneau, *Compt. rend.*, 143, 127 (1906), gives the b. p. as 137–138" and the m. p. of the semicarbazone as 98" whiie Blaise, *Ann. chim. phys.*, [8] 17,371 (1909), gives the m. p, as 92°.

[p] Bromine and potassium permanganate tests. No semicarbazone.

[q] Prepared from the olefin made by dehydrating the carbinol with iodine.

[r] The bromination was at −3° to prevent charring; time. 110 hrs

[s] Meerwein, *Ann.*, 396, 255 (1913). gives the b. p. as 130.6° (760 mm.), and the m. p. of the semicarbazone as 136–138°.

[t] Considerable amounts of mono- and polybromides were obtained.

"When hydrolysis with water alone gave no satisfactory result, the experiment was repeated with lead oxide and water.

compound to the 1,2-dibromo compound by bromination in the presence of ferric bromide gave mainly polybromides. The monobromide was then treated with potassium hydroxide in methyl alcohol to give a 45% yield of 2-methylbutene-1, b. p. 33–35.5° (740 mm.). This was treated with bromine in carbon tetrachloride to give an 80% yield of the desired dibromide, 1,2-dibromo-2-methylbutane, b. p. 60–62° (15 mm.).

Seventy grams (0.30 mole) of this dibromide was refluxed with 700 cc. of distilled water in a 1-liter flask provided with a 50-cm. column. The distillate on redistillation gave only 7 g. of material of b. p. 94-98' (735 mm.). This had an aldehyde odor, reduced ammoniacal silver nitrate and gave a semicarbazone, m. p. 85–93" which could not be purified by recrystallization. The product of the hydrolysis was thus impure methylethylacetaldehyde.

2,3-Dibromo-2-methylbutane.—This bromide was best prepared from tertiary amyl alcohol (b. p. 100–102° (740 mm.)[8] and bromine at 60–65°. The yield of material of

b. p. 56–60° (20 mm.) was 75%.[9] The bromide was also prepared by the direct addition of bromine at 5° to trimethylethylene prepared by dehydrating tertiary amyl alcohol with 15% sulfuric acid. The use of a solution of bromine in aqueous sodium bromide solution was also tried. Neither of these methods had any advantage over the direct treatment of tertiary amyl alcohol with pure bromine. The dibromide (1740 g.) was hydrolyzed with stirring, first refluxing and later distilling off the methyl isopropyl ketone. The product on redistillation through a 90 × 1.5 cm. packed column weighed 477 g., b. p. 90–93.4° (734 mm.), n^{20}_{D} 1.3880, yield 55% based on the tertiary amyl alcohol used. A small amount of high boiling material, b. p. 69–82° (29 mm.), n^{20}_{D} 1.4630. 42.6% bromine, with strong lachrymatory power was obtained.

The results with the other twelve dibromides are summarized in Table I.

Summary

1. The hydrolysis and rearrangement of isobutylene dibromide and trimethylethylene dibromide are practical methods of converting tertiary butyl and tertiary amyl alcohols to isobutyraldehyde and methyl isopropyl ketone in good yields.

2. The hydrolysis of thirteen other dibromides prepared from aliphatic tertiary alcohols has been studied. With seven of these the rearranged aldehyde or ketone has been obtained in poor yield. With the others, polymerizations occur apparently due to the formation of substituted butadienes and other unsaturated products.

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[9] Full details of the preparation of the dibromide and of its hydrolysis to methyl isopropyl ketone will appear in "Organic Syntheses," Vol. XIII, 1933.

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Researches on Pyrimidines. CXXXI. The Reduction of 1,2,3,4-Tetrahydropyrimidines

BY KARL FOLKERS[1] AND TREAT B. JOHNSON

Several new members of a hitherto little studied class of tetrahydropyrimidines were described in a recent publication from this Laboratory.[2] These were represented by the general formula, I, in which R designates an alkyl, aryl or arylalkyl group. Inasmuch as the investigation of these compounds was primarily to ascertain whether they were of pharmacological interest, it was desirable to hydrogenate a few of them to the hexahydropyrimidine derivative, II, if possible, and then to determine the effect on the physiological activity. Furthermore, these hexahydropyrimidines possessing an ureide structure could probably be hydrolyzed to substituted β,β-diamino-isobutyric acids, III, which in themselves would be interesting substances and otherwise difficult to obtain.

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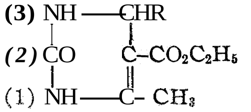
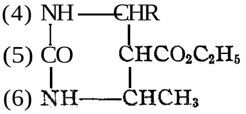
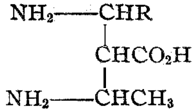
[1] Squibb and Sons Research Fellow in Organic Chemistry.

[2] Folkers, Harwood and Johnson. THIS JOURNAL, 54, 3751 (1932).


I


II


III

In contrast to the large amount of published work on keto-pyrimidines, there is relatively little literature on the more reduced pyrimidine structures. Over colloidal palladium or platinum, the 5,6 double bond of uracil was quite resistant to reduction at 20–25°, but at 75° it was reduced to dihydrouracil.[3] The reduction of the 5,6 double bond of N-1-methyl-6-phenyluracil-N-3-acetic acid or its methyl ester could not be accomplished at 20–25° with a colloidal palladium catalyst. Hydrogen iodide was also ineffective.[4] Hilbert[5] found that the 5,6 double bond of uracil-4-ethyl acetate and 3-methyl-uracil could be hydrogenated with Adams platinum catalyst at 20–25°, but the rate was very slow.

The only reduction experiment on a pyrimidine of type I was made by Biginelli,[6] the discoverer of the reaction leading to the formation of these compounds. He reported that 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, IV, when treated with sodium amalgam, yielded, in addition to unaltered material, a compound of m. p. 229–230° which he believed to be the hexahydropyrimidine derivative, and another solid melting at 59–60°. Biginelli's analysis of the higher melting compound indicated the adsorption of one mole of hydrogen, whereas the hydrogen content of the lower melting one was high for an additional mole of hydrogen.

Although his directions for the sodium amalgam reduction were incomplete, attempts were made to duplicate them, but they were without satisfactory results. The use of 2.5% sodium amalgam in glacial acetic acid was also without success, for 94.1% of the compound was recovered unaltered. Neither did hydrogen iodide effect reduction. Two grams of the pyrimidine dissolved in 200 ml. of ethanol was unaffected in the presence of 0.15 g. of platinum catalyst after four hours. However, by using a large amount of catalyst and glacial acetic acid as solvent, hydrogenation was effected. The drop in pressure indicated the absorption of 3 moles and the product, which melted at 237.5–238.5°, was shown by analysis to contain six more atoms of hydrogen. Since these experimental conditions do not give reduction of the carbamido- or carbethoxy groups, and excluding cleavage, the benzenoid nucleus must have been reduced while the double bond of the pyrimidine ring remained intact. This product, 2-keto-4-cyclohexyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, dissolved

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(3) Johnson and Brown, *Proc Nat. Acad. Sci.*, 7, 75 (1920); Brown and Johnson, THIS JOURNAL, 45, 2702 (1923).

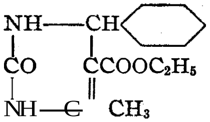
(4) Evans and Johnson, *ibid.*, 62, 5000 (1930).

(5) Hilbert *ibid.*, 64, 2078 (1932).

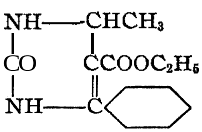
(6) Biginelli, *Gazz. chim. ital.*, 23, [1] 366 (1893).

in glacial acetic acid would not absorb more hydrogen in the presence of a large amount of fresh catalyst and over a long period of time at 20–25°. Since a temperature of 75° facilitated reduction in ethanol solvent of the uracil series, this pyrimidine was tested under these conditions. However, there was not the slightest reduction of 2 g. of the 4-cyclohexyl derivative dissolved in 200 ml. of ethanol after forty-two hours at 60–75° in the presence of 0.57 g. of platinum catalyst.

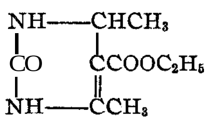
It seemed probable then that the compound of m. p. 229–230° obtained by Biginelli was one containing a partially hydrogenated benzenoid nucleus. Such reduction has been quite widely accomplished by the use of sodium.[7] It is to be noted in the above-mentioned papers on uracil derivatives that reduction of the 5,6-double bond caused a marked drop in the melting point, whereas Biginelli's reduction raised the melting point. In reference to Biginelli's product of m. p. 59–60°, he stated that it was probably a mixture of two isomeric hexahydropyrimidines, the one of m. p. 229–230° and another which had not been obtained pure. This seemed unlikely since his hydrogen analysis was 0.27–0.31% high and the fact that he stated the substance, on long contact with water, decomposed to emanate an odor of benzaldehyde, an observation which indicates the tetrahydro rather than the hexahydropyrimidine structure.



M. p. 206–208°
IV



M. p. 165–166.5°
V



M. p. 192.5–193.5°
VI

Possibly the normal resistance to reduction of the 5,6-double bond of pyrimidine IV was enhanced by the nature and number of the groups present on this portion of the pyrimidine nucleus, for usually highly substituted structures are more difficult to hydrogenate than the unsubstituted ones. For a single example, 1-alkyl-4-piperidones have been hydrogenated in five to eight hours by the Adams platinum catalyst, but the sole substitution of a carbethoxy group in the 3 position of the piperidine nucleus decreased the rate of hydrogenation to fifty hours.[8] Undoubtedly, the resistance to reduction would also be partially dependent on the actual position of the groups. So it was of interest to hydrogenate the isomer of pyrimidine IV in which the methyl and phenyl groups are interchanged, or 2-keto-4-methyl-5-carbethoxy-6-phenyl-1,2,3,4-tetrahydropyrimidine, V.[9]

(7) Houben, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1925, Vol. II, p. 326.

(8) Bolyard and McElvain, THIS JOURNAL, 51, 923 (1929).

(9) The preparation of this pyrimidine from urea, acetaldehyde and benzoylacetic ester is described in the experimental part of this paper, and demonstrates further applicability of this type of condensation. Furthermore, since no conversion of the isomers IV and V has been noticed, the 5,6 double bond of this structure must be somewhat stable.

The product of this reduction showed that both the 5,6 double bond and the benzenoid nucleus were reduced, and demonstrated the dependence of double bond reduction on position in the cycle. Besides the analysis of the product, the presence of the hexahydropyrimidine ring was further indicated by saponification to the carboxylic acid derivative. Treatment of these tetrahydropyrimidines IV with alcoholic alkali results in rupture of the pyrimidine ring, but reduction of the 5,6-double bond stabilizes the ring so that the corresponding pyrimidine-5-carboxylic acids are obtainable on hydrolysis.

An attempt to hydrogenate 2-keto-4,6-dimethyl-5-carbethoxy-1,2,3,4-tetrahydropyrimidine, VI, was made to determine if replacing the phenyl group by an alkyl group would alter the resistance of the 5,6-double bond to reduction. This substance, in common with the other pyrimidines of this series, was too insoluble in ethanol at 20–25° to allow the use of this solvent. In 150 ml. of glacial acetic acid there was no reduction of 9.9 g. of this pyrimidine during nine hours in the presence of 0.62 g. of platinum catalyst. Even after standing thirty-eight hours, it was demonstrated that the catalyst still possessed some degree of activity for, after releasing the pressure and decanting the solution, it effected complete reduction of 0.1 mole of maleic acid in 200 ml. of glacial acetic acid in forty-five minutes.

The selective reduction of the benzenoid nucleus over the 5,6-pyrimidine double bond in compound IV made it of interest to hydrogenate a compound in which the two rings were separated by one or two carbon atoms. For this purpose, 2-keto-4-phenylethyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, VII, was selected.

Thayer and McElvain[10] have reported the reduction over the Adams platinum catalyst of certain 1-R-4-piperidones in which R was the phenyl, benzyl or phenylethyl group. This catalyst at 20–25° effected the reduction of both the aromatic nucleus and keto group when R was phenyl, and when R was benzyl the net result was apparently the same, but with a retarded rate of nuclear hydrogenation. When the two nuclei were separated by two carbon atoms, as when R was phenylethyl, only the keto group underwent reduction.

The 4-phenylethylpyrimidine, VII, on the absorption of three moles of hydrogen gave a product which melted sharply at 192.5–193.5°, and, as shown below, must be the result of aromatic nucleus reduction. The 4-styrylpyrimidine derivative, VIII, on hydrogenation to completion absorbed four moles and gave a product of m. p. 192.5–193.5° which by analysis was shown to contain eight additional atoms of hydrogen, or only enough to reduce completely the styryl group. The mixed melting point of the complete reduction products of the 4-phenylethyl and 4-styryl derivatives was 192.5–193.5°, so they both must be the 4-β-cyclohexylethyl-

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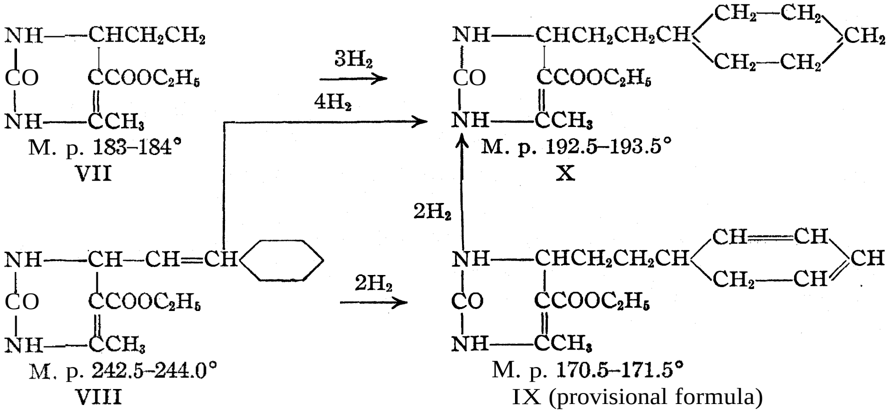
(10) Thayer and McElvain, THIS JOURNAL, 49, 2862 (1927).

tetrahydropyrimidine derivative, X. Therefore, this separation of benzenoid and pyrimidinoid nuclei did not alter their selective reduction.



M. p. 183–184° VII

M. p. 192.5–193.5° X

M. p. 242.5–244.0° VIII

M. p. 170.5–171.5° IX (provisional formula)

The rate of hydrogenation of the 4-styryl derivative was unusually interesting. Two moles of hydrogen were quickly absorbed in ten minutes, whereas the last two were absorbed over a period of three hours. The experiment was repeated and stopped at the perceptible break in the absorption rate. It was found that this used catalyst was still active enough to carry the reduction of another sample to the same point, thus demonstrating the ease of the absorption of the first two moles. The intermediate product obtained in all cases melted sharply at 170.5–171.5°, and was shown by analysis to contain four additional hydrogen atoms. The sharpness of its melting point and its lack of change on recrystallization indicate it to be a pure substance. Hydrogenation of other phenylpyrimidines interrupted after adsorption of integral moles of hydrogen gave products, evidently mixtures, which melted over a 5 to 8° range and changed on recrystallization. On further reduction this intermediate product absorbed two more moles of hydrogen to give the product first obtained which melted at 192.5–193.5°. Since all the hydrogen absorbed by this 4-styrylpyrimidine derivative was used only in saturating the four double bonds of the styryl group, it seemed most probable that the ethylenic double bond and the adjacent double bond in the benzenoid nucleus absorb the first two moles of hydrogen as a conjugated system, or through a simultaneous catalytic reaction. The two following considerations also indicate that the two double bonds are not independent of one another in their reduction or that in any case the particular activation which precedes the formation of this intermediate is derived from the chemical and physical characteristics of this 4-styryl derivative.

First, by interrupting the hydrogenation of the 4-phenylethyl derivative at the absorption of one mole, a product was obtained which melted at 171.5–180° and apparently was a mixture. Therefore, this molecule which contained one of the double bonds already saturated could not attain the necessary state of activation. Indeed, one does not expect direct catalytic hydrogenation of simple benzene nuclei to produce easily pure di- or tetrahydro derivatives, although such hydrogenation of condensed benzene nuclei is common.

Second, the rapid and continuous absorption of the first two moles of hydrogen, together with the conception of the possible mechanisms leading to the intermediate, would not lead one to expect to isolate a pure compound if the process were interrupted after the absorption of one mole. This was found to be true, for a mixture melting at 191–200° resulted from allowing the 4-styryl derivative to absorb one mole of hydrogen. In this experiment the amount of catalyst was decreased in order that the primary process or processes would be more distinct.

Further data on these pyrimidines will be made available through their absorption spectra measurements which are being carried out at Mount Holyoke College under the direction of Professor Emma P. Carr.

Experimental Part

The reductions discussed in this paper were carried out under 3 atmospheres' pressure in the usual hydrogenation apparatus, and with the Adams platinum catalyst.[11]

The **2-keto-4-R-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidines** in which R was the phenyl, methyl, phenylethyl or styryl groups have already been described.[12]

Table I contains a summary of the data on the various hydrogenations. After filtration of the catalyst, the products were precipitated by pouring the filtrates into 500–1000 ml. of water. After washing, the products were recrystallized from dilute alcohol or by dissolving in an excess of alcohol and distilling to incipient crystallization. The yields express the pure products, the loss being that of one to three recrystallizations. The actual amount hydrogenated in each case was chosen so that the total absorption would be an integral number (3–7) of gage scale divisions in order that the pressure drop could be more accurately interpreted. All melting points were taken with a standardized thermometer. The catalyst did not seem to accumulate poisons from these reductions so that it could be reworked and used again successfully. The carbon and hydrogen analyses were micro determinations carried out in the laboratory of Dr.-Ing. A. Schoeller, Berlin-Schmargendorf, Tolzerstrasse 19, Germany. The nitrogen analyses were macro Kjeldahl determinations.

2-Keto-4-methyl-5-carbethoxy-6-phenyl-1,2,3,4-tetrahydropyrimidine, V.—Three grams of urea, 3.3 g. of acetaldehyde, and 12 g. of ethyl benzoylacetate were added to 25 ml. of glacial acetic acid (10°) and then heated on a steam-bath for twenty hours, after which four drops of concentrated hydrochloric acid from a 5-ml. pipet were added, and the heating continued for another twenty-four hours. After cooling, the solution was poured into 200 ml. of water. After several days the oil was removed by long suction from the solid which slowly formed. The cake was washed with 50% alcohol; crude yield, 6.2 g. After several recrystalliiations from dilute alcohol, crystals were obtained of the constant m. p. 165–166.5".

Anal. (micro) Calcd. for $C_{14}H_{16}N_2O_3$: C, 64.58; H, 6.20; N, 10.77. Found: C, 64.53; H, 6.26; N (micro), 10.97, 10.85.

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(11) "Organic Syntheses," John Wiley and Sons, New York, 1932, Coll. Vol. I, pp. 55, 452.

(12) Folkers. Harwood and Johnson, THIS JOURNAL, 54, 3751 (1932).

TABLE I

HYDROGENATION OF 2-KETO-4-R-5-CARBETHOXY-6-METHYL-1,2,3,4-TETRAHYDROPYRIMIDINES

	R =	Amt., mole	Catalyst, g.	Glacial acetic acid, ml.	Hydrogen, mole	Time, hrs.
1	Phenyl-	0.05	0.70	125	0.15	6.5
2	Phenyl-	.05	.32	150	.05	4.0
3	Phenyl-	.05	.40	150	.15	24.0
4	Cyclohexyl-	.05	.70	150		8.0
5	Phenylethyl-	.025	.40	200	.025	2.0
6	Phenylethyl-		.70	100	.050	1.0
7	Styryl-	.025	.70	150	.10	3.2
8	Styryl-	.025	.20	150	.050	0.33
9	Styryl-	.025	.10	150		0.13
10	2-Dihydrophenylethyl-	.025	.70	130	.050	0.66

	Product R =	M. p., °C.	Yield, %		Analysis, % C	H	N	
	Cyclohexyl	237.5–238.5	64.7	Calcd.	63.11	8.33	10.52	
				Found	63.30	8.34	10.37	10.38
2	Mixture	192.5–193.5						
3	Cyclohexyl	237.5–238.5						
4	Cyclohexyl	237.5–238.5						
5	Mixture	171.5–180						
6	2-Cyclohexylethyl	192.5–193.5	65.3	Calcd.	65.25	8.90	9.52	
				Found	65.41	9.00	9.50	9.41
7	2-Cyclohexylethyl	192.5–193.5	84.4					
8	2-Dihydrophenyl-ethyl	170.5–171.5	94.5	Calcd.	66.16	7.60	9.65	
				Found	66.36	7.73	9.46	9.41
9	Mixture	191–200						
10	2-Cyclohexylethyl	192.5–193.5						

2-Keto-4-methyl-5-carbethoxy-6-cyclohexylhexahydropyrimidine.—Six and one-half grams of pyrimidine V was dissolved in 100 ml. of glacial acetic acid and shaken with 0.7 g. of catalyst under three atmospheres for twenty-four hours. After catalyst filtration, practically all the acetic acid was distilled under diminished pressure below 50°, and the residue was poured into 175 ml. of cold water to precipitate the product. After recrystallization from alcohol and water, a melting point of 110–172" showed that reduction was not complete. Hydrogenation was repeated using 0.5 g. of fresh catalyst. After drying to constant weight at 60° and 23 mm., the product now melted at 179–181° and was not changed after four recrystallizations. It was 2-keto-4-methyl-5-carbethoxy-6-cyclohexylhexahydropyrimidine.

Anal. (micro) Calcd. for $C_{14}H_{24}N_2O_3$: C, 62.63; H, 9.01; N, 10.44. Calcd. for $C_{14}H_{22}N_2O_3$: C, 63.11; H, 8.33; N, 10.52. Found: C, 62.94, 62.76; H, 8.90, 9.01; N (micro), 10.31; N (macro), 10.23, 10.05.

2-Keto-4-methyl-5-carboxylic acid-6-cyclohexyl-hexahydropyrimidine.—Thirteen-hundredths gram of the above ester was refluxed for forty minutes with 25 ml. of 0.15 N alcoholic alkali. The solution, after dilution and acidification with hydrochloric acid, was distilled until all ethanol had been removed. On cooling the residue, the acid crystallized, m. p. 290–291° with decomposition. The melting point did not change after recrystallization from dilute alcohol.

Anal. Calcd. for $C_{12}H_{20}N_2O_3$: C, 59.96; H, 8.39; N, 11.66. Found: C, 59.71; H, 8.36; N, 11.00.

Summary

I. The behavior of some 2-keto-4-alkyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidines on catalytic reduction has been investigated.

2. It has been shown that the 5,6-double bond in such pyrimidine combinations is very resistant to change.

3. In all cases examined the 4-aryl groups were attacked by hydrogen in the presence of the catalyst and reduced to the corresponding hexahydro or saturated structure.

4. In only one case examined, namely, 2-keto-4-methyl-5-carbethoxy-6-phenyl-1,2,3,4-pyrimidine, where phenyl is substituted on carbon adjacent to the 5,6-double bond, did we succeed in reducing the 5,6-double bond in the pyrimidine ring.

5. The pharmacological behavior of these highly reduced structures is now under investigation.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

A Study of the Toxicity of Rotenone Hydrochloride, Acetylrotenone and Rotenolone Using the Goldfish as the Test Animal[1]

BY W. A. GERSDORFF

The toxicological examination of derivatives of rotenone and related compounds with the use of the goldfish as the test animal has been continued in this Laboratory with the threefold hope of discovering a material more toxic and more stable than rotenone, and at the same time securing data by which a correlation may be made between the toxicity and chemical structure. The method used by the author has been described in a previous paper[2] and studies by that method of some of the compounds have also been published.[3,4] This paper presents the results of a similar examination of rotenone hydrochloride, acetylrotenone and rotenolone prepared in the Insecticide Division of the Bureau of Chemistry and Soils.

Rotenone hydrochloride (m. p. 193°) was prepared from rotenone by H. L. Haller according to the method of S. Takei.[5] The compound is formed by the addition of hydrochloric acid at the double bond of the

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(1) Presented before the Division of Agricultural and Food Chemistry at the Meeting of the American Chemical Society, Denver, Colo., August 22-26, 1932.

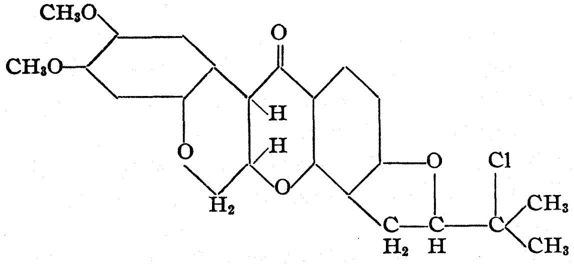
(2) Gersdorff, THIS JOURNAL, 52, 3440-3445 (1930).

(3) Gersdorff, *ibid.*, 52, 5051-5056 (1930).

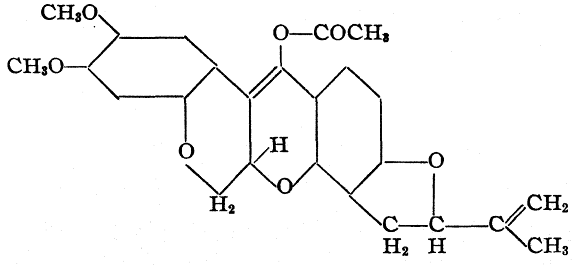
(4) Gersdorff, *ibid.*, 53, 1897-1901 (1931).

(5) Takei, *Ber.*, 61B, 1003-1007 (1928).

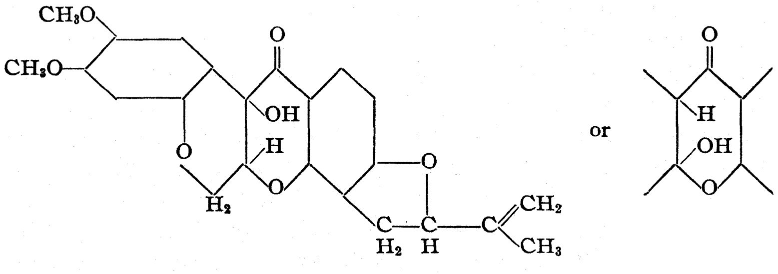
tubaic acid side chain. Its structure, now that the formula for rotenone has been established,[6] is shown by the formula



Acetylrotenone (m. p. 135°) was prepared[7] by the treatment of rotenone with acetic anhydride. The compound is an enol acetate as shown by its formula



Rotenolone (m. p. 140–141°) was prepared[8] by the saponification of the acetate obtained as one of the products of the reaction of iodine on a hot alcoholic solution of rotenone and potassium acetate. The hydroxyl group replaces the hydrogen attached to one of the adjacent asymmetric carbon atoms of rotenone, as



Which of these two formulas is correct has not yet been established.

The two lots of fishes used in these tests were slightly larger than the fishes used for the determination of the toxicity curves for rotenone and some of its derivatives in 1930,[3] and apparently somewhat more resistant

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(6) LaForge and Haller, THIS JOURNAL, 64, 810-818 (1932).

(7) Smith and LaForge, *ibid.*, 54, 2996–3000 (1932).

(8) LaForge and Smith, *ibid.*, 52, 1091-1098 (1930).

as shown in Table I. In this, comparisons are made of the three lots of fishes at two concentrations of rotenone.

TABLE I

RESISTANCE OF THREE LOTS OF GOLDFISHES TO ROTENONE AT 27°

Lot no. of fishes	Concn., mg. per liter	No. of fishes used	Mean wt. of fishes, g.	Mean survival time, min.
1	0.10	12	2.3	95
2	.10	5	2.4	114
3	.10	8	2.4	123
1	.05	11	2.2	150
2	.05	10	2.7	180
3	.05	12	2.3	177

TABLE II

TOXICITY OF ROTENONE HYDROCHLORIDE TO GOLDFISH AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
0.50	9	41	2.2	128	0.83
.33	12	41	2.2	125	.89
.20	9	40	2.1	124	.84
.17	12	41	2.2	127	.87
.10	13	41	2.2	130	.82
.050	11	41	2.2	138	.74
.033	9	42	2.3	181	.60
.025	11	43	2.4	212	.51
.020	18	42	2.3	273	.46
.015	7	42	2.3	386	.28
.0050	10	[b]	[b]	Eight fishes, 980[c], two still active after 72 hrs.	.12[c]
.0025	11	[b]	[b]	Apparently unaffected, 72 hrs.	

[a] Estimated from length. [b] Fishes not measured, but of same approximate size. [c] These figures are only approximate since a large number of fishes would be required to give an accurate mean value. The reciprocal of the survival time of a fish surviving the test is taken as zero, since the reciprocal of any survival time longer than the test would be negligibly small.

The rotenone curves were obtained from tests made with fishes from lot number 1, the acetylrotenone and rotenolone curves from lot number 2, and the rotenone hydrochloride curves from lot number 3. Lots 2 and 3 are considered identical since the differences fall within experimental error.

The toxicity data are given in Tables II to IV. The survival time curves and the velocity of fatality curves, which were plotted from these data, are given in Fig. 1 and 2.

Comparative data obtained from the velocity of fatality curves are given in Table V. In each case the straight line which is an approximation of that portion of the curve corresponding to the greatest rate of increase in the velocity of fatality with increase in concentration is prolonged to cut the x-axis at a point designated a; the slope of this line is designated tan θ.

TABLE III

TOXICITY OF ACETYLROTENONE TO GOLDFISH AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
0.50	12	44	2.6	98	1.08
.25	12	42	2.3	96	1.06
.15	8	47	3.1	120	0.87
.10	20	43	2.4	180	.60
.075	19	42	2.3	229	.49
.050	16	44	2.6	362	.31
.025	14	43	2.4	Ten fishes. 365[c]. Four fishes still active after 48 hrs.	.20[c]
.020	8	37 (5)	1.6	Five fishes, 904'. Three fishes still active after 30 hrs.	.13[c]
.015	6	41	2.2	One small fish, 670'. five fishes still active after 49 hrs.	.02[c]
.010	7	[b]	[b]	Two small fishes affected at first but apparently recovered. *All* active after 27 hrs.	

a, b and *c* as in Table II.

TABLE IV

TOXICITY OF ROTENOLONE TO GOLDFISH AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
3.0	8	41	2.2	118	0.89
2.0	13	43	2.4	122	.84
1.5	24	42	2.3	136	.80
1.0	23	43	2.4	143	.72
0.75	18	44	2.6	178	.59
.50	7	45	2.7	199	.52
.40	13	42	2.3	250	.42
.30	7	40	2.1	358	.28
.25	15	41	2.2	448	.26
.10	6	43 (4)	2.4	856[c]	.12[c]
.050	10	[b]	[b]	Apparently unaffected in 52 hrs.	

a, b and *c* as in Table II.

TABLE V

COMPARATIVE TOXICITY AT 27° OF ROTENONE HYDROCHLORIDE, ACETYLROTENONE AND ROTENOLONE TO GOLDFISH

Substance	a[a], mg. per liter	Tanθ[b] liters per mg. per min.	Minimum surv. time, min.
Rotenone hydrochloride	<0.002	0.22	125
Acetylrotenone	< .002	.067	95
Rotenolone	.020	.011	115

[a] The theoretical threshold of toxicity, *i.* e., the concentration necessary to just kill. [b] The rate of increase of the theoretical velocity of fatality with increase in concentration. These values express the volume of water which must be added, throughout this portion of the curve, to any solution containing one milligram of the toxic substance in order to increase the survival time one minute.

In this way values are obtained for the theoretical threshold of toxicity, that is, the concentration below which the substance does not cause death, and the rate of increase of the theoretical velocity of fatality with increase in concentration. The minimum survival time is approximated from the original data when the higher concentration portion of the survival time curve has become practically a horizontal line. This is assumed to occur

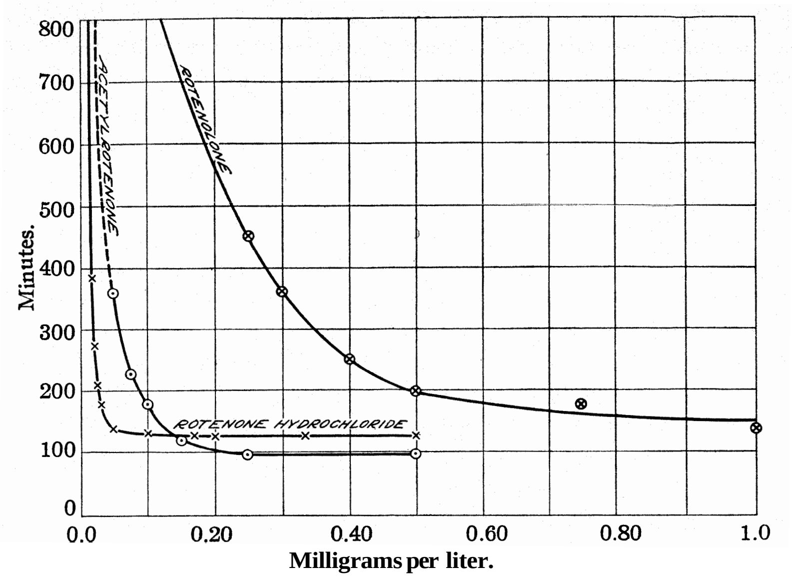

Fig. 1.—Survival time curves.

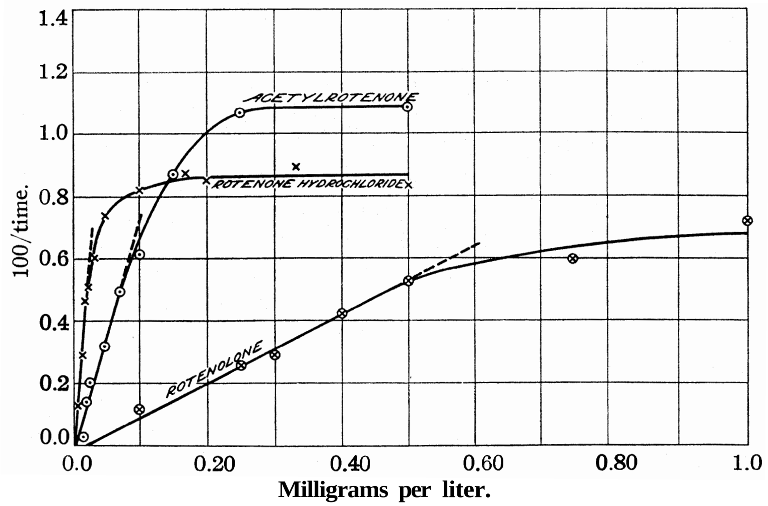

Fig. 2.—Velocity of fatality curves.

when the survival times corresponding to concentrations, one of which is double the other, do not differ by more than 5%. The values are probably a little higher than that of the asymptote but they will serve for a practical comparison of the substances at this portion of their curves.

It was pointed out, when Powers' formula $\sqrt{\tan \Theta/a}$ was first used as a measure of the relative toxicities of substances,[3] that this formula[9] was not all that could be desired since the effect of the threshold value was thought to be too great and *a* third factor, the toxicity at the high concentrations as expressed by the portion of the survival time curve closely approaching the horizontal asymptote (corresponding therefore to the minimum survival time), was not considered at all. In the present study, these points are emphasized even more, since by use of this formula rotenone hydrochloride appears to have a toxicity ten times that of rotenone and even acetylrotenone appears to have a toxicity somewhat greater than rotenone. These values do not express the true relationship as shown by the curves. The former express the relationship between the toxicities of the substances only at their thresholds of toxicity and immediately beyond and may be misleading as a comparative guide for pest control work in which the toxic concentrations used are likely to be on or near the horizontal limb of the survival time curve. The use of this formula is therefore discontinued. It is still hoped that by obtaining toxicological data on other related compounds and by developing, if possible, a criterion more suitable for the expression of relative toxicity, the effect of a change in chemical structure on toxicity may be expressed arithmetically as well as graphically.

Conclusions

Solutions of rotenone hydrochloride and acetylrotenone become toxic to goldfish at very low concentrations, less than 0.002 mg. per liter, but with solutions of rotenolone the theoretical threshold of toxicity is 0.020 mg. per liter. The theoretical velocity of fatality of rotenone hydrochloride increases with increase in concentration at a higher rate than do those of acetylrotenone and rotenolone (about three and one-third and twenty times as much, respectively). The minimum survival times of these three substances, in the order, acetylrotenone, rotenolone and rotenone hydrochloride are ninety-five, one hundred and fifteen and one hundred and twenty-five minutes.

WASHINGTON, D. C.

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(9) Powers, *Ill. Biol. Mono.*, 4 (2) (1917).

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

The Condensation of 2-Butanone with Normal Aliphatic Aldehydes[1]

BY S. G. POWELL, HAZEL C. MURRAY AND MAYNARD M. BALDWIN

In a previous paper[2] it was shown that when 2-butanone reacts with n-butyraldehyde the condensation takes place through the methylene group of the ketone. This is also the case in its reaction with formaldehyde[3] and acetaldehyde.[4] On the other hand Thoms and Kahre[5] have shown that the reaction between 2-butanone and isobutyraldehyde yields 2-methyl-3-heptene-5-one, $(CH_3)_2CHCH{=}CHCOC_2H_5$. In view of this difference in behavior it seemed desirable to investigate the reaction between 2-butanone and other aldehydes.

It was found that the condensation of 2-butanone with propionaldehyde, n-valeraldehyde and n-heptaldehyde takes place through the methylene group of the ketone. From these results and those previously obtained in the cases of formaldehyde, acetaldehyde and n-butyraldehyde, it appears that the normal aliphatic aldehydes in general react in this manner with 2-butanone. As Thoms and Kahre have shown that the branched-chain isobutyraldehyde brings about a different reaction, an investigation of the reaction between 2-butanone and other branched-chain aldehydes is now under way.

The constitution of the condensation product was determined in each case by dehydration of the aldol to the unsaturated ketone and reduction of this to the corresponding saturated alcohol. In the case of propionaldehyde this saturated alcohol was found to be identical with the 3-methyl-2-hexanol described by Bjelouss[6] and on oxidation yielded a ketone identical with the 3-methyl-2-hexabone obtained by the hydrolysis of ethyl methyl-n-propyl-acetoacetate. The structures of the alcohols obtained from n-valeraldehyde and n-heptaldehyde were determined by oxidation and identification of the resulting acids as n-valeric and enanthic acids, respectively.

The condensation. dehydration, reduction to the saturated alcohol, and oxidation of this to the saturated ketone were carried out as described in the previous paper.[2]

In Table I are listed the new compounds prepared.

Identification of the Acids Obtained by Oxidizing 3-Methyl-2-octanol and 3-Methyl-2-decanol.—The alcohols were oxidized by boiling with a

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[1] This paper is based in part upon theses presented by Hazel C. Murray and Maynard M. Baldwin in partial fulfilment of the requirements for the Master's degree. Original manuscript received January 19, 1931.

(2) Powell, Tars JOURNAL, 46, 2514 (1924).

(3) U. S. Patent 981,668.

(4) Salkind, J. *Russ. Phys.-Chem. Soc.*, 37, 484 (1905).

(5) Tkoms and Kahre, Arch. *Pharm.*, 263, 241 (1925).

(6) Bjelouss, *Ber.*, 45, 625 (1912).

TABLE I

	B. p., °C.	Mm.	n_D	d_4	Yield, %	Analyses, % Calcd C	Analyses, % Calcd H	Analyses, % Found C	Analyses, % Found H
$C_2H_5CHOHCH(CH_3)COCH_3$	94–96	20	1.435 (24°)	0.939 (22°)	61	64.57	10.84	64.00	10.95
$C_4H_9CHOHCH(CH_3)COCH_3$	98	16	1.4404 (29°)	.9167 (29°)	35	68.31	11.47	68.46	11.61
$C_6H_{13}CHOHCH(CH_3)COCH_3$	147	23	1.4425 (21°)	.889 (22°)	50	70.90	11.91	70.53	12.07
$C_3H_7CH(CH_3)COCH_3$	142-145		1.409 (24°)	.828 (25")	57	73.61	12.37	73.53	12.60
$C_5H_{11}CH(CH_3)COCH_3$	64-65	18	1.424 (27°)	.832 (27")	52	75.98	12.75	75.36	12.39
$C_7H_{15}CH(CH_3)COCH_3$	121	20	1.431 (20°)	.823 (20°)	43	77.57	13.03	77.20	12.84
$C_5H_{11}CH(CH_3)CHOHCH_3$	75	15	1.437 (27°)	.831 (27°)	47	75.00	13.88	74.91	13.98
$C_7H_{15}CH(CH_3)CHOHCH_3$	125	19	1.440 (21°)	.834 (23°)	43	76.65	14.05	76.10	13.36

mixture of sodium dichromate and sulfuric acid. The water-insoluble acid obtained from 3-methyl-2-octanol boiled at 183° (uncorr.); b. p. of n-valeric acid is 185". Titration with standard alkali gave equivalent wt. 102; calcd. for valeric acid, 100.

The water-insoluble acid obtained from 3-methyl-2-decanol boiled at 220° (corr.); b. p. of enanthic acid is 224". The amide, obtained by treatment with thionyl chloride and then ammonia, melted at 95° as did a mixture of it with enanthamide.

The water-soluble acid in each case was identified as acetic acid by conversion into the *p*-bromophenacyl ester by the method of Reid and Judefind.[7]

Summary

1. 2-Butanone has been found to react with propionaldehyde, n-valeraldehyde and *n*-heptaldehyde through the methylene group.

2. Several new derivatives of 3-methylhexane, 3-methyloctane and 3-methyldecane have been prepared.

SEATTLE, WASHINGTON

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[7] Reid and Judefind, THIS JOURNAL, 42, 1083 (1920).

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

The Reaction of Organic Halides with Piperidine. III. Cyclohexyl Bromide and the Butyl Bromides

BY W. V. DRAKE AND S. M. MCELVAIN

In the first paper[1] of this series cyclohexyl bromide was found to differ very markedly from other secondary bromides both in the rate and the course of its reaction with piperidine. It was suggested then that the greater reactivity of the open chain secondary bromides might be due to their rearrangement to the more reactive primary structure, a transformation which cyclohexyl bromide cannot undergo without rupture of a carbon to carbon linkage. The validity of this hypothesis has now been tested by an investigation of the tertiary amines produced in the reaction of piperidine with cyclohexyl bromide and each of the four butyl bromides. This work has led to the isolation of four different N-butyl-piperidines, a result which definitely shows that the above explanation for the relative inertness of cyclohexyl bromide has no experimental justification.

Experimental

Materials Used.—The piperidine and petroleum ether were prepared as previously described.[1] Isobutyl bromide was prepared according to Noller[2] and cyclohexyl bromide by the procedure of Kamm and Marvel.[3] n-Butyl, *sec*-butyl and tert-butyl bromides were prepared by the Norris procedure.4 The tertiary butyl alcohol which was used melted at 22–25°.[5]

General Procedure

The procedure which has been described[1] for carrying out the reaction of piperidine with various alkyl bromides was used with the following modifications: (a) the larger quantities of reactants used in the work now reported required Pyrex bomb tubes instead of test-tubes for the reaction; (b) the temperature of the reaction was raised to 150–155" in order that a greater amount of reaction might take place within a given time; (c) after removal of the piperidine hydrobromide, the unreacted piperidine was precipitated as piperidine thiocarbamate[6] with carbon bisulfide;[7] (d) when all of the

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(1) Semb and McElvain, THIS JOURNAL, **53, 690 (1931).**

(2) Noller, *ibid.*, **53, 635 (1931).**

(3) "Organic Syntheses," **Vol.** I, **1921,** p. **1.**

(4) Norris, Am. Chem. J., **38, 639 (1907).**

(5) In some earlier experiments tertiary butyl alcohol melting at 10–16° was used to prepare the bromide. This bromide, however. gave a tertiary amine hydrochloride which after recrystallization gave analyses corresponding to a N-propylpiperidine hydrochloride. By comparison with an authentic specimen, this hydrochloride was found to be N-isopropylpiperidine hydrochloride, m. p. 272–273°; Cl, calcd.: 21.67; found, 21.64. This compound undoubtedly resulted from small amounts of isopropyl alcohol in the tertiary butyl alcohol. The tertiary amine hydrochloride prepared from tertiary butyl alcohol, m. p. 22–25', not only gave correct analyses, but when mixed with N-isopropylpiperidine hydrochloride melted at 260–264°.

(6) Ladenburg and Roth, *Ber.*, **17, 514 (1884).**

(7) This procedure was found to give just as satisfactory results as the one using phenyl isocyanate as a precipitant for the unreacted piperidine.[1] The handling of the carbon bisulfide precipitate was the same as that used for piperidinoformanilide. Several precipitations of known quantities of piperidine from a petroleum ether solution by carbon bisulfide showed that 95% of the piperidine could be recovered.

piperidine had been removed from the petroleum ether solution the tertiary amine was precipitated as the hydrochloride with dry hydrogen chloride. These hydrochlorides then were recrystallized from an alcohol–ether mixture.

Table I summarizes the pertinent data which were obtained. Column A shows the amount of piperidine used with each bromide. A relatively large amount of reactants was necessary in the case of tertiary butyl bromide in order that sufficient tertiary amine could be obtained. The ratio of one mole of the bromide to two moles of piperidine was used in each reaction. Column C shows the moles of piperidine hydrobromide which precipitated from the reaction; therefore the percentages in parentheses indicate the extent of each reaction. Column D shows the amounts of piperidine precipitated by carbon bisulfide as piperidine thiocarbamate and the percentage values in parentheses are based on one-half of the piperidine used. Column E gives the yields in moles and percentage of the tertiary amines. Column F shows the amounts in moles and the percentage of the total piperidine used which was accounted for as piperidine hydrobromide, piperidine thiocarbamate and N-alkylpiperidine hydrochloride.

TABLE I

REACTION OF PIPERIDINE WITH VARIOUS ALKYL BROMIDES AT 150–155°

	A	B	C	D	E	F
Alkyl group	Moles × 10 piperidine used	Reaction time, hr.	Moles × 10 piperidine hydrobromide (%)	Moles × 10 unreacted piperidine (%)[a]	Moles × 10 tertiary amine hydrochloride (%)	Total piperidine recovered C + D + E (%)
n-Butyl	0.4	48	0.20 (100)	0.00	0.179 (89)	0.379 (95)
Sec-butyl	0.4	48	0.195 (98)	.027 (13)	.154 (77)	0.376 (94)
Isobutyl	0.4	48	0.193 (98)	.00	.180 (90)	0.373 (93)
Tert-butyl	2.4	48	1.11 (92)	.838 (70)[b]	.036 (3)	1.982 (83)
Cyclohexyl	0.8	120	0.386 (97)	.267 (67)	.111 (28)	0.764 (95)

[a] Determined as piperidine thiocarbamate by precipitation with carbon bisulfide. [b] This value is probably low because of the pressure developed in the reaction tube and consequent loss of piperidine when the tube was opened and this pressure released.

The properties and analyses of the tertiary amine hydrochlorides (Column E, Table I) are summarized in Table II.

TABLE II

N-ALKYLPIPERIDINE HYDROCHLORIDES[a]

			Analyses, %					
			Calcd.			Found		
Alkyl group	Formula	M. p., °C.	C	H	Cl	C	H	Cl
n-Butyl	$C_9H_{20}NCl$	239–240	60.81	11.35	19.96	60.80	11.22	19.98
Sec-butyl	$C_9H_{20}NCl$	208–209	60.81	11.35	19.96	61.01	11.25	20.02
Isobutyl	$C_9H_{20}NCl$	257–258[b]	60.81	11.35	19.96	60.75	11.40	19.93
Tert-butyl	$C_9H_{20}NCl$	268–269[b]	60.81	11.35	19.96	60.75	11.26	20.14
Cyclohexyl	$C_{11}H_{22}NCl$	292–293[b]	64.33	10.90	17.49	64.40	10.93	17.44

[a] These compounds were obtained by recrystallization of the hydrochlorides of Column E, Table I, from an alcohol–ether mixture. The recovery of the recrystallized products varied from 65–85%. It is believed that these recrystallization losses were largely manipulative. [b] These compounds melt with decomposition.

The free tertiary amines were isolated from the above hydrochlorides in the cases of *n*-butyl, *sec*-butyl and isobutyl piperidine. The amounts of N-tertiary-butylpiperidine hydrochloride obtained from the reaction of tertiary butyl bromide were so small that the isolation of the free base was not attempted.[8] The properties and analyses of these tertiary amines are given in Table III.

TABLE III

N-BUTYLPIPERIDINES

N substituent	B. p., °C. (740 mm.)	d^{25}_{25}	n^{25}_{D}	N analyses, % Calcd.	N analyses, % Found
n-Butyl[a]	171–172	0.8210	1.4442	..	..
Sec-butyl	169–170	.8334	1.4468	9.92	9.73
Isobutyl[b]	160–161	.8161	1.4382	9.92	9.87

[a] This compound has been reported by Gibson and Macbeth [*J. Chem. Soc.*, 119, 438 (1921)] as boiling at 170–172°. [b] Hjortdahl, *Jahresb.*, 1085 (1882), reports the chloroplatinate of this amine.

Discussion of the Results

It is seen from Tables I and II that four different N-butylpiperidines are formed from the reaction of piperidine with the four butyl bromides. This fact seems to be definite proof that these bromides react to form tertiary amines without previous rearrangement. A comparison of the data for secondary butyl bromide and cyclohexyl bromide given in Table I shows that the difference in behavior of these secondary bromides is one of degree rather than kind. When the reaction of secondary butyl bromide with piperidine is forced practically to completion, a yield of tertiary amine lower than those from the primary butyl bromides is obtained and the amount (13%) of unreacted piperidine (Column D) shows that some loss of hydrogen bromide to form the unsaturated hydrocarbon has taken place. This latter reaction is confirmed by the fact that the petroleum ether solution, after removal of the unreacted piperidine, rapidly decolorizes a bromine solution. Cyclohexyl bromide also shows these two types of reaction, only in this case the relative amounts of tertiary amine formation and loss of hydrogen bromide are the reverse of those obtained from secondary butyl bromide. On the basis of these data the results reported in the first paper[1] of this series do not appear anomalous. It should be noted that the tertiary amines are formed directly from the reaction of the bromide with piperidine rather than through the addition of the latter compound to the unsaturated hydrocarbon, since it was found that the substitution of cyclohexene for cyclohexyl bromide gave no isolable quantity of tertiary amine under the same conditions of reaction that produced a 28% yield of the tertiary amine from the bromide.

(8) Velghe [*Bull. Sci. Acad. Roy. Belg.*, [5] 11, 301 (1925); *Chem. Abstracts*, 20, 1053 (1926)] reports N-tertiary-butylpiperidine, b. p., 166°, from the reaction of a-piperidinoisobutyronitrile with methylmagnesium bromide.

Noller and Dinsmore,[9] in a recent study of the reaction of alkyl bromides with pyridine, have shown that the loss of hydrogen bromide and the formation of alkyl pyridinium bromides are distinct, but simultaneously occurring reactions. It is quite probable also that in the reaction of alkyl halides with secondary amines the relative rates of two independent reactions, the loss of halogen acid and tertiary amine formation, determine the course of the reaction, since the data for the reaction of alkyl bromides with piperidine in Table I appear, in general, to be quite similar to those reported by Noller and Dinsmore.

Summary

The isolation of four different N-butylpiperidine hydrochlorides from the reaction of piperidine with the butyl bromides has demonstrated that these bromides, in this reaction, do not rearrange previous to reaction. The difference between the behavior of cyclohexyl bromide and other secondary bromides has been found to be one of degree rather than kind.

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(9) Noller and Dinsmore, THIS JOURNAL, 54, 1025 (1932).

MADISON, WISCONSIN

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Diarsyls. V. Reactions of Tetraphenyldiarsyl

BY F. F. BLICKE, R. A. PATELSKI AND L. D. POWERS

Tetraphenyldiarsyl reacts with sulfur to form tetraphenylarsyl sulfide; with sulfur chloride, diphenylchloroarsine and sulfur were obtained; with thionyl chloride the reaction products were diphenylchloroarsine, sulfur dioxide and sulfur.

Bromocyanogen and the diarsyl yield diphenylbromoarsine; triphenylarsine is formed when the diarsyl reacts with phenylmagnesium bromide.

Interaction with arsenic trichloride proceeds rapidly with the formation of diphenylchloroarsine and arsenic in practically quantitative yield; when phenylarsine oxychloride was used the reaction products were diphenylchloroarsine and phenylarsine oxide.

Phosphorus trichloride and the diarsyl yield diphenylchloroarsine.

Tetraphenyldiarsyl, dissolved in benzene, was shaken with liquid sodium–potassium alloy. The colorless benzene layer soon became intensely yellow-brown in color and a very decided change was noticed in the appearance of the alloy, a change which we attribute to the formation of the potassium, or sodium derivative of diphenylarsine. Bromobenzene was added to the mixture and, after some time, evaporation of the benzene layer yielded oily triphenylarsine; the latter was isolated in the form of the methyl iodide addition product, methyltriphenylarsonium iodide, since this substance is easier to purify, in small amounts, than triphenylarsine.

Each of the following compounds which contain reactive halogen attached to carbon was mixed with tetraphenyldiarsyl, dissolved in benzene, and allowed to remain at room temperature for twelve hours: acetyl chloride, benzoyl chloride, benzophenone chloride, 2,4-dinitrobromobenzene and tetraphenyldichloroethane.[1] In each instance approximately 80% of unchanged diarsyl was recovered.

It was thought possible that ethylene oxide might react with tetraphenyldiarsyl, dissolved in benzene, to form diphenyldiphenylarsyloxyethylarsine, $(C_6H_5)_2As-CH_2CH_2-O-As(C_6H_5)_2$; the diarsyl, however, was recovered unchanged.

Tetraphenyldiarsyl is not affected by cold halogen acids or alkali.

Experimental Part

All of the reactions described below were carried out in a free-radical bulb in an atmosphere of nitrogen. Absolute grades of alcohol and ether were used and all solvents were saturated with nitrogen prior to use.

Unless otherwise indicated the tetraphenyldiarsyl was prepared from 3.56 g. (0.01 mole) of diphenyliodoarsine, 1 cc. of mercury and 90 cc. of dry benzene. The mixture was shaken for twelve hours and then siphoned through a filter into a radical bulb. It has been shown previously that by this method a yield of at least 90% of pure diarsyl is obtained. All of the yields of the various reaction products described below were calculated on the assumption that 0.01 mole of the iodoarsine yielded 0.009 mole of the diarsyl.

Sulfur.—To the diarsyl solution there was added 0.15 g. of sulfur, dissolved in carbon disulfide. After twenty-four hours the solvents were removed by distillation under reduced pressure, the oily residue dissolved in ether, the solution poured into a beaker and concentrated. Tetraphenylarsyl sulfide separated in crystalline condition. The yield was 1.9 g.; calcd. yield 2.2 g.; mixed m. p. 61–62°[2] after recrystallization from alcohol.

Sulfur Chloride.—The diarsyl solution was mixed with 0.67 g. of sulfur chloride dissolved in 20 cc. of benzene. The mixture became opalescent at once and a tan-colored precipitate of sulfur soon formed. After twenty-four hours the benzene solution was rose colored, due probably to the presence of sulfur in a colloidal state. The mixture was filtered, all of the solvent removed and the crystalline residue dissolved in alcohol. Upon concentration of the alcoholic solution 1.8 g. of diphenylchloroarsine was obtained; calcd. yield 2.4 g.; m. p. 42–43°.[3]

The reaction takes place equally well in ether but in this instance the solution does not become pink in color.

Thionyl Chloride.—Six-tenths of a gram of thionyl chloride, dissolved in 20 cc. of benzene, was allowed to react with the diarsyl solution. The same observations were made as recorded in the preceding experiment. There was obtained 1.8 g. of diphenylchloroarsine; calcd. yield 2.4 g.; m. p. 42–43°.

Bromocyanogen.—The solution of the diarsyl was treated with 1.06 g. of bromocyanogen,[4] dissolved in 20 cc. of benzene. After four days a small amount of a tan-colored precipitate, presumably polymerized cyanogen, had formed. The mixture was filtered, the solvent removed from the filtrate and the residue recrystallized from alcohol.

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(1) Finkelstein, *Ber.*, 43, 1533 (1910).

(2) Michaels. Ann., 321, 141 (1902).

(3) Blicke and Smith, THIS JOURNAL, 51, 1564 (1929).

(4) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 11.

The product, diphenylbromoarsine, melted at 52–53°.[3] The yield was 2.2 g., calcd. yield 2.8 g.

Phenylmagnesium Bromide.—Phenylmagnesium bromide, obtained from 4.81 g. of bromobenzene, 0.72 g. of magnesium and 20 cc. of ether, was added to the diarsyl solution. After twelve hours the mixture was removed from the radical bulb and decomposed with ice and ammonium chloride. The benzene-ether layer was shaken with sodium hydroxide solution, the aqueous layer separated and the organic solvents removed. The gummy residue was triturated with petroleum ether (30–60°) in order to dissolve the triphenylarsine and the solvent allowed to evaporate from the petroleum ether extract. The residue was treated with warm 95% alcohol, the alcoholic solution concentrated and inoculated with a crystal of triphenylarsine. After the material had become crystalline it was recrystallized from alcohol; m. p. 60–61°;[5] yield 1 g.

Arsenic Trichloride.—A solution prepared from 0.70 g. of arsenic trichloride and 20 cc. of benzene, was added to the diarsyl solution. The mixture became cloudy immediately and a red brown, amorphous precipitate of arsenic formed.[6] After twelve hours the mixture was filtered, the solvent removed from the filtrate and the residue recrystallized from alcohol. The product, diphenylchloroarsine, melted at 41–42°; yield 2.3 *g.;* calcd. yield 2.4 g.

Phenylarsine Oxychloride.—One and two-tenths grams of phenylarsine oxychloride,[7] dissolved in 90 cc. of dry benzene, was added to the diarsyl. A transitory lavender color was noticed. After several hours the solution was concentrated, poured into a beaker and all of the solvent removed. When the oily residue was rubbed under ether it became crystalline and the diphenylchloroarsine dissolved in the solvent while the phenylarsine oxide remained undissolved. The ether solution was decanted and the process repeated until a complete separation had been effected. There was obtained 1.9 g. of diphenylchloroarsine; m. p. 41–42°; calcd. yield 2.4 g. The phenylarsine oxide weighed 0.73 g.; m. p. 144–147°; calcd. yield 0.74 g.

Phosphorus Trichloride.—The benzene was removed from the diarsyl solution and after the solid material had been dissolved in 90 cc. of carbon tetrachloride there was added 0.46 g. of phosphorus trichloride, dissolved in 20 cc. of carbon tetrachloride. After twelve hours the solvent was removed, the yellow, oily residue treated with ether and after some time the solution was filtered from insoluble material. The diphenylchloroarsine obtained from the ether solution was recrystallized from alcohol; yield 0.6 g.; mixed m. p. 3741°.

Sodium–Potassium Alloy.—Liquid sodium–potassium alloy, prepared under xylene from 1.2 g. of sodium and 1.0 g. of potassium, was washed free from the liquid medium and added to the diarsyl solution. After the mixture had been shaken for twelve hours it consisted of a yellow-brown benzene layer, black, suspended particles and unchanged alloy. There was then added 12.2 g. of bromobenzene. The mixture became warm and after it had been shaken for three hours it was filtered, the solvent removed from the filtrate and the red-brown gummy residue subjected to steam distillation in order to remove biphenyl. Since the product could not be obtained in a solid state it was refluxed with 3 cc. of methyl iodide for several hours in order to convert the triphenylarsine into methyltriphenylarsonium iodide. The latter was obtained in the form of crystals contaminated by an oil. The material was extracted with hot water and the aqueous solution boiled with charcoal. The methyltriphenylarsonium iodide obtained from the filtrate weighed 1.6 g.; mixed m. p. 72–73°.[8]

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(5) Sachs and Kantorowicz [*Ber.*, 41, 2788 (1908)] recorded the melting point as 60.5°.

(6) The precipitate was dissolved in nitric acid, the solution evaporated to dryness and the residue treated with hydrochloric acid; when hydrogen sulfide was passed into the solution yellow arsenious sulfide was obtained.

(7) Michaelis, *Ann.*, 201, 202 (1880).

(8) Michaelis, *ibid.*, 821, 166 (1902).

Summary

It has been shown that tetraphenyldiarsyl reacts readily with the following substances: sulfur, sulfur chloride, thionyl chloride, bromocyanogen, phenylmagnesium bromide, arsenic trichloride, phenylarsine oxychloride, phosphorus trichloride and sodium–potassium alloy.

Compounds which contain reactive halogen attached to carbon, such as acetyl chloride, benzoyl chloride, benzophenone chloride, 2,4-dinitrobromobenzene and tetraphenyldichloroethane, as well as ethylene oxide, do not react with the diarsyl, in benzene solution, at ordinary temperature.

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A Study of Phenyl- and Diphenylarsine

BY F. F. BLICKE AND L. D. POWERS

Phenylarsine, dissolved in bromobenzene, absorbs oxygen very rapidly at first; the absorption then proceeds at a slower rate until the material has absorbed approximately one molecular equivalent of the gas. When the arsine was exposed to air we obtained the same oxidation products mentioned by Dehn[1] but the relative amounts varied in different experiments. Phenylarsine and sulfur react to form phenylarsine sulfide and hydrogen sulfide.

It has been reported[2] that phenylarsine reacts with iodine, dissolved in potassium iodide solution, to yield phenylarsonic acid and phenyldiiodoarsine. It has been shown that two molecular equivalents of this arsine, dissolved in ether, reacts instantly with four molecular equivalents of iodine to form phenyldiiododiarsine in quantitative yield. However, when only two molecular equivalents of iodine are used arsenobenzene is formed and by the use of three equivalents diphenyldiiododiarsyl is obtained.

Equimolecular quantities of phenylarsine and triphenylarsine dichloride react in accordance with the following equation

$$2C_6H_5AsH_2 + 2(C_6H_5)_3AsCl_2 = 2(C_6H_5)_3As + C_6H_5As{=}AsC_6H_5 + 4HCl$$

Dehn and Wilcox[3] reported that diphenylarsine, when allowed to oxidize in air, was converted almost completely into diphenylarsinic acid; a very small amount of tetraphenylarsyl oxide was also obtained. We found that diphenylarsine, dissolved in bromobenzene, absorbs oxygen as rapidly as a solution of triphenylmethyl or tetraphenyldiarsyl. The quantity of oxygen absorbed was approximately that required for the interaction of the arsine

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(1) Dehn, *Am. Chem. J.*, *33*, 149 (1905).

(2) Dehn, *ibid.*, 33, 161 (1905); Fleury, Bull. *soc.* chim., [4] **27**, 490 (1920).

(3) Dehn and Wilcox, *Am. Chem. J.*, *36*, 47 (1906).

with two molecular equivalents of the gas. Diphenylarsinic acid was isolated as an oxidation product in 93% yield.

It might be expected that the initial product of oxidation would be the unstable diphenylhydroxyarsine, $(C_6H_5)_2As(OH)$, which would decompose spontaneously into tetraphenylarsyl oxide. Diphenylarsinic acid might then be formed as the result of further oxidation of this substance. However, this explanation of the formation of diphenylarsinic acid cannot be correct since tetraphenylarsyl oxide, dissolved in bromobenzene, remains unchanged after long contact with oxygen; hence it seems that the acid is not produced through the intermediate formation of the oxide.[4]

It has been stated by Dehn and Wilcox[5] that diphenylarsine, dissolved in ether, reacts with iodine to form diphenyliodoarsine. It has been shown that the latter compound is obtained from equimolecular amounts of the arsine and iodine; however, if one molecular equivalent of iodine is added to two equivalents of the arsine, tetraphenyldiarsyl is produced; the diarsyl may have been formed as the result of the action of diphenyliodoarsine on diphenylarsine.[6]

Since tetraphenyldiarsyl and iodine react instantly[7] to form diphenyliodoarsine, the mechanism of the formation of diphenyliodoarsine from diphenylarsine and iodine is uncertain; the iodoarsine might be produced by direct replacement of the arsine hydrogen by iodine or as the result of the action of iodine on tetraphenyldiarsyl.

Diphenylarsine and tetraphenylarsyl oxide react in alcohol to form tetraphenyldiarsyl in excellent yield. The arsine and tetraphenylarsyl sulfide react in an analogous manner.

It was found that the chlorine as well as the ethoxy group in phenylchloroethoxyarsine was removed when the latter reacted with diphenylarsine; diphenylchloroarsine and arsenobenzene were isolated as reaction products.

$$2(C_6H_5)_2AsH + 2C_6H_5AsCl(OC_2H_5) = 2(C_6H_5)_2AsCl + C_6H_5As{=}AsC_6H_5 + 2C_2H_5OH$$

When the arsine was allowed to react with triphenylbromomethane in a molecular equivalent amount, diphenylbromoarsine and triphenylmethane were produced.

With triphenylmethyl the arsine yielded triphenylmethane and tetraphenyldiarsyl.

It was found that interaction of triphenylarsine dichloride with two molecular equivalents of diphenylarsine yields triphenylarsine and tetraphenyldiarsyl (A), while equimolecular amounts of the two compounds react to produce triphenylarsine and diphenylchloroarsine (C). It is possible in the latter instance that tetraphenyldiarsyl is formed as an intermediate

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(4) Phenylarsine oxide, likewise, dissolved in bromobenzene does not absorb oxygen.

(5) Ref. 3, p. 45.

(6) Blicke and Powers, THIS JOURNAL, 54, 3358 (1932).

(7) Blicke and Smith, *ibid.*, 51, 2276 (1929).

A $(C_6H_5)_3AsCl_2 + 2(C_6H_5)_2AsH = (C_6H_5)_3As + (C_6H_5)_2As{-}As(C_6H_5)_2 + 2HCl$

B $(C_6H_5)_3AsCl_2 + (C_6H_5)_2As{-}As(C_6H_5)_2 = (C_6H_5)_3As + 2(C_6H_5)_2AsCl$

C $2(C_6H_5)_3AsCl_2 + 2(C_6H_5)_2AsH = 2(C_6H_5)_3As + 2(C_6H_5)_2AsCl + 2HCl$

product and that this substance then reacts with triphenylarsine dichloride according to formulation B. At least we have shown in a separate experiment that the arsine dichloride and the diarsyl react to yield triphenylarsine and diphenylchloroarsine.

Equimolecular amounts of diphenylarsine and triphenylarsine hydroxychloride react, undoubtedly, in accordance with formulation F. A separation of the compounds formed, however, was not found possible until the mixture of reaction products had been treated with alkali, which converted the diphenylchloroarsine into tetraphenylarsyl oxide. The arsine, oxide and chloride in formulation F are probably produced as a result of the interaction of diphenylarsine and the hydroxychloride with the formation of triphenylarsine and tetraphenyldiarsyl (D); tetraphenyldiarsyl and the hydroxychloride then react to yield tetraphenylarsyl oxide, diphenylchloroarsine and triphenylarsine (E). In separate experiments we have shown that the reactions formulated (D and E) take place readily.

D $4(C_6H_5)_2AsH + 2(C_6H_5)_3As(OH)Cl = 2(C_6H_5)_3As + 2(C_6H_5)_2As{-}As(C_6H_5)_2 + 2HCl + 2H_2O$

E $2(C_6H_5)_2As{-}As(C_6H_5)_2 + 2(C_6H_5)_3As(OH)Cl = (C_6H_5)_2As{-}O{-}As(C_6H_5)_2 + 2(C_6H_5)_2AsCl + 2(C_6H_5)_3As + H_2O$

F $4(C_6H_5)_2AsH + 4(C_6H_5)_3As(OH)Cl = 4(C_6H_5)_3As + (C_6H_5)_2As{-}O{-}As(C_6H_5)_2 + 2(C_6H_5)_2AsCl + 3H_2O + 2HCl$

Experimental Part

All reactions were carried out in a modified free-radical bulb[8] at ordinary temperature and all compounds sensitive toward oxygen were isolated in a carbon dioxide atmosphere. Melting points of compounds which react with oxygen were determined in a sealed tube filled with nitrogen.

Although it was evident that some of the reactions took place rapidly and were, no doubt, completed in a short time, all of the reaction mixtures were shaken for at least twelve hours unless otherwise indicated.

Absolute grades of alcohol and ether were used and all solvents were thoroughly saturated with nitrogen prior to use.

Reactions of Phenylarsine

Oxygen.—In a typical experiment 0.543 g. of the arsine, dissolved in bromobenzene, absorbed 57 cc. (N. T. P.) of oxygen in one minute, 66 cc. in sixty minutes and 81 cc. after forty-eight hours. Interaction of the above amount of arsine with one molecular equivalent of oxygen would require 79 cc. of oxygen.

Sulfur.—To 3.5 g. (2.6 cc.) of phenylarsine, dissolved in 10 cc. of benzene, there was added 0.64 g. of sulfur, dissolved in 50 cc. of the same solvent. After twenty-four hours all of the solvent was removed; during this process a strong odor of hydrogen sulfide was noticeable. The oily residue was dissolved in 20 cc. of benzene. Upon the addition

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(8) Ref. 6, p. 3356.

of 50 cc. of absolute alcohol the phenylarsine sulfide precipitated in crystalline form; yield 0.81 g.; calcd. yield 1.8 g.; m. p. 161–163°.[9]

Iodine.—The iodine was decolorized at once when 2.54 g. (0.01 mole) of iodine, dissolved in 40 cc. of ether, was added to 1.54 g. (1.14 cc., 0.01 mole) of phenylarsine, dissolved in 10 cc. of ether, and an orange, crystalline precipitate separated. This material was arsenobenzene contaminated by a small amount of by-product, probably diphenyldiiododiarsyl. The mixture was shaken for forty-eight hours and then treated with alkali. After separation of the alkaline layer and removal of the solvent, 1 g. of arsenobenzene was obtained; calcd. yield 1.5 g. After recrystallization from toluene the product melted at 208–210°.

To 1.54 g. (0.01 mole) of the arsine, dissolved in ether, there was added 3.81 g. (0.015 mole) of iodine, dissolved in 75 cc. of the same solvent. Diphenyldiiododiarsyl crystallized slowly from the solution. The ether was decanted and the product washed three times with ether. The yield was 2.5 g.; calcd. yield 2.8 g.; m. p. 175–177°.[10]

To a solution prepared from 1.54 g. (0.01 mole) of the arsine and 10 cc. of benzene, there was added 5.1 g. (0.02 mole) of iodine, dissolved in 80 cc. of benzene. The iodine was decolorized immediately. The red oil, phenyldiiodoarsine, obtained after complete removal of the solvent, was isolated as phenylarsylene N-pentamethylenedithiocarbamate; the yield of the latter was 4.6 g.; calcd. yield 4.7 g.; m. p. 183–184°.[11]

Triphenylarsine Dichloride.—A solution prepared from 3.77 g. (0.01 mole) of triphenylarsine dichloride and 40 cc. of dry benzene was added to 1.54 g. (0.01 mole) of phenylarsine, dissolved in 10 cc. of the same solvent. After a short time the stopcock of the radical bulb was opened for an instant in order to allow hydrogen chloride to escape. The mixture was shaken and after twelve hours the liquid was decanted from the precipitated arsenobenzene into a second radical bulb. The residue of arsenobenzene was suspended in ether and shaken with alkali in order to remove traces of hydrogen chloride,[12] and then with alcohol and ether; yield 0.9 g.; calcd. yield 1.5 g.; mixed m. p. 210–212°.[13]

The decanted benzene solution was shaken with alkali and the benzene was then removed. The oily, yellow residue was boiled with 50 cc. of alcohol and the alcoholic solution filtered in air. When the filtrate cooled triphenylarsine precipitated. A further amount of product was obtained from the filtrate; yield 2.5 g.; calcd. yield 3.1 g.; m. p. 60–61°.[14]

Reactions of Diphenylarsine

Oxygen.—The data obtained from two typical experiments are as follows: 0.565 g. of the arsine, dissolved in bromobenzene, absorbed 49 cc.[15] of the gas in one minute and 58 cc. in sixty minutes. If the arsine reacted with two molecular equivalents of oxygen, 55 cc. would be required. In another experiment 0.868 g. of arsine absorbed 89 cc. of the gas after sixty minutes; calcd, amount, 85 cc. Extraction with ammonia

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[9] The melting point recorded for this compound by Schulte [*Ber.*, 15, 1953 (1882)] is 152°. It was reported [Blicke and Smith, THIS JOURNAL, 52, 2948 (1930)] that preparation of the sulfide from phenyldichloroarsine and hydrogen sulfide yielded material which melted at 174–176°. When this experiment was repeated, sulfide was obtained which melted at 162–164°. Mixed with the sulfide obtained from phenylarsine the mixed melting point was found to be 162–164°. It is not strange that different samples of phenylarsine sulfide possess different melting points in view of the fact that marked variations in melting point have been observed among preparations of phenylarsine oxide.

[10] Blicke and Smith, THIS JOURNAL, 52, 2943 (1930).

[11] Blicke and Oakdale, *ibid.*, 54, 2995 (1932). Due to an error the melting point was recorded previously as 173–174°.

[12] Arsenobenzene absorbs oxygen rapidly in the presence of halogen acids [Blicke and Smith. *ibid.*, 52, 2946 (1930)].

[13] Michaelis and Schafer [*Ber.*, 46, 1742 (1913)] recorded the m. p as 212°.

[14] The m. p. has been recorded as 58–59° by Pfeiffer [*ibid.*, 37, 4621 (1904)].

[15] About two-thirds of this volume was absorbed after fifteen seconds.

water of the combined bromobenzene solutions yielded 1.51 g. or 93% of the calcd. amount of diphenylarsinic acid; m. p. 168–170°.[16]

Iodine.—When 2.30 g. (0.01 mole) of diphenylarsine reacted with 2.54 g. (0.01 mole) of iodine in 50 cc. of alcohol, a light yellow solution was obtained which yielded 3.60 g. of diphenyliodoarsine; m. p. 41–42°.[17] The calcd. yield is 3.56 g.

To 2.30 g. (177 cc., 0.01 mole) of diphenylarsine, dissolved in 10 cc. of absolute alcohol, there was added 1.27 g. (0.005 mole) of iodine, dissolved in 40 cc. of alcohol. The iodine was decolorized instantly and crystals of tetraphenyldiarsyl began to separate rapidly. The alcohol was decanted, the product suspended in about 25 cc. of ether and shaken with water until hydriodic acid had been completely removed. The water layer was separated and most of the ether removed by distillation under reduced pressure. The diarsyl was then washed three times with 10-cc. portions of absolute alcohol and dried in a bath at 60–70° under diminished pressure. The material melted at 127–129°;[18] yield 2.0 g.; calcd. yield 2.3 g. Dissolved in bromobenzene 0.769 g. of the compound absorbed 40 cc. (N. T. P.) of oxygen; calcd. absorption 37 cc.

Tetraphenylarsyl Oxide.—To 3.45 g. (0.015 mole) of diphenylarsine, dissolved in 20 cc. of absolute alcohol, there was added 3.56 g. (0.0075 mole) of tetraphenylarsyl oxide, dissolved in 80 cc. of the same solvent. After several days, the solvent was decanted from the precipitated tetraphenyldiarsyl and the latter washed four times with 20-cc. portions of alcohol; yield 6.25 g. or 91% of the calcd. amount; m. p. 125–127°. Dissolved in bromobenzene 1.378 g. of the material absorbed 65 cc. of oxygen in less than two minutes; calcd. absorption 67 cc.

Tetraphenylarsyl Sulfide.—Tetraphenyldiarsyl began to crystallize from the solution soon after the addition of 2.45 g. of tetraphenylarsyl sulfide, dissolved in alcohol, to 2.30 g. of diphenylarsine, dissolved in 20 cc. of the same solvent. The alcohol was decanted from the diarsyl, the latter washed twice with alcohol and then with ether; m. p. 129–130°; yield 1.9 g.; calcd. yield 4.6 g.

Phenylchloroethoxyarsine.—To 4.6 g. of phenylchloroethoxyarsine (0.02 mole), dissolved in 80 cc. of absolute alcohol there was added 4.60 g. (0.02 mole) of diphenylarsine, dissolved in 20 cc. of the same solvent. Arsenobenzene began to precipitate at once in crystalline form. The precipitate was filtered through a Jena filter, in an inert atmosphere,[19] and washed with four 50-cc. portions of alcohol. The alcohol washings were added to the alcoholic filtrate. Finally, the arsenobenzene was washed thoroughly with absolute ether; m. p. 208–209°; yield 2.83 g.; calcd. yield 3.04 g.

From the alcoholic filtrate 4.7 g. of diphenylchloroarsine was obtained; mixed m. p. 40–42°; calcd. yield 5.3 g.

Triphenylbromomethane.—Two and three-tenths grams (0.01 mole) of diphenylarsine and 3.23 g. of triphenylbromomethane dissolved in 70 cc. of ether were placed in a free-radical apparatus. After twenty-four hours the solution was concentrated to a small volume. Ten cc. of petroleum ether (30–60°) was added and the solution cooled, whereupon a small amount of fairly pure triphenylmethane separated in crystalline form. After recrystallization from alcohol the methane melted at 91–93°;[20] mixed m. p. 92–93°. The ether–petroleum ether filtrate was evaporated to dryness, the residue dissolved in ether and filtered to remove traces of diphenylarsinic acid. After evaporation of the solvent from the filtrate, the crystalline residue was dissolved in a small amount of

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(16) We are inclined to believe that the m. p. 178° assigned to this substance by Bart [*Ann.*, 429, 101 (1922)] is too high. We have observed in many instances that the acid melts in the neighborhood of 170° and this corresponds to the observation of Gibson and Johnson [*J. Chem. Soc.*, 99 (1928)] who stated that an analyzed sample of the acid melted at 171°.

(17) Blicke and Smith, THIS JOURNAL, 51, 1564 (1929).

(18) Blicke, Weinkauff and Hargreaves, *ibid.*, 52, 782 (1930).

(19) In the presence of diphenylchloroarsine arsenobenzene absorbs oxygen rapidly.

(20) Kekulé and Franchimont, *Ber.*, 5, 907 (1872).

hot alcohol. When the solution was cooled, practically pure triphenylmethane separated. Concentration of the filtrate yielded diphenylbromoarsine, mixed m. p. 52–54°,[21] and upon further concentration a mixture which seemed to consist of the methane and bromoarsine was obtained The components of this mixture were not separated. In all there were isolated 1.7 g. of pure methane and 0.7 g. of pure bromoarsine.

Triphenylmethyl.—To 4.6 g. (0.02 mole) of diphenylarsine in 10 cc. of benzene there was added a solution of triphenylmethyl prepared from 6.5 g. of triphenylbromomethane, 10 g. of molecular silver and 80 cc. of benzene. The orange triphenylmethyl solution was decolorized at once. After concentration to a volume of 20 cc. triphenylmethane precipitated in the form of its benzene addition product; the benzene-free crystals, which weighed 1.6 g., melted at 90–92°. The solution was decanted from the crystals into a second radical bulb, the solvent removed and the residue recrystallized from alcohol. The tetraphenyldiarsyl obtained weighed 1.0 g.; m. p. 125–128". Dissolved in bromobenzene 0.776 g. of the material absorbed 39 cc. (N. T. P.) of oxygen; calcd. amount 38 cc.

Triphenylarsine Dichloride (A, C).—A mixture of 3.77 g. (0.01 mole) of the arsine dichloride dissolved in 40 cc. of dry benzene and 4.60 g. (0.02 mole) of the arsine dissolved in 10 cc. of benzene was shaken for twelve hours, the benzene removed completely and 40 cc. of absolute alcohol added to the residue to dissolve the triphenylarsine formed. The alcoholic solution was decanted, the residue of tetraphenyldiarsyl washed with alcohol and then recrystallized from 200 cc. of the same solvent; yield 4.1 g.; calcd. yield 4.6 g.; m. p. 130–131°. Dissolved in bromobenzene 1.045 g. of the diarsyl absorbed 53 cc. of oxygen in ten seconds; calcd. absorption 51 cc. Upon concentration of the alcoholic solution of triphenylarsine 2.1 g. of the latter compound was obtained; calcd. yield 3.0 g.; m. p. 60–61°.

A mixture of 3.77 g. (0.01 mole) of triphenylarsine dichloride, dissolved in 40 cc. of dry benzene, and 2.30 g. (0.01 mole) of diphenylarsine yielded triphenylarsine and diphenylchloroarsine. Since it was found impossible to separate these compounds, the mixture was treated with sodium hydroxide solution, whereby the diphenylchloroarsine was converted into tetraphenylarsyl oxide. The latter substance is quite insoluble in petroleum ether (30–60°) while the triphenylarsine is very soluble in this solvent. After the separation had been effected, the triphenylarsine was recrystallized from alcohol; yield 2.3 g.; calcd. yield 3.1 g.; mixed m. p. 60–61°. The yield of tetraphenylarsyl oxide was 2.0 g.; calcd. yield 2.4 g.; mixed m. p. 92–94°.[22]

Tetraphenyldiarsyl and Triphenylarsine Dichloride (B).—To 2.62 g. of tetraphenyldiarsyl, dissolved in 30 cc. of dry benzene, there was added 1.72 g. of triphenylarsine dichloride, dissolved in 30 cc. of the same solvent. After twelve hours the solvent was removed completely and the residue of triphenylarsine and diphenylchloroarsine dissolved in 20 cc. of petroleum ether (30–60°). The diphenylchloroarsine was separated in the form of tetraphenylarsyl oxide as described above. The yield of the latter product was 1.9 g.; calcd. yield 2.7 g.; m. p. 92–95". The yield of triphenylarsine was 1.2 g.; calcd. yield 1.7 g.; m. p. 59-60°.

Triphenylarsine Hydroxychloride (D, F).—When 4.60 g. (0.02 mole) of diphenylarsine, dissolved in 20 cc. of absolute alcohol, was added to 3.58 g. (0.01 mole) of triphenylarsine hydroxychloride, dissolved in 20 cc. of the same solvent, tetraphenyldiarsyl precipitated immediately while triphenylarsine remained in solution. After twelve hours the alcoholic solution was decanted from the crystalline material into a second radical bulb. The diarsyl was washed with absolute alcohol and then recrystallized from 150 cc. of this solvent. The yield was 3.6 g.; calcd. yield 4.6 g.; m. p.

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(21) Steinkopf and Schwen, Ber., **54**, 1459 (1921).

(22) The highest m. p. recorded in the literature is 95.5–96.5° [Blicke and Smith, THIS JOURNAL, **51**, 1562 (1929)].

127–129°. Dissolved in bromobenzene 0.839 g. of the diarsyl absorbed 43 cc, (N. T. P.) of oxygen; calcd. absorption 41 cc. The triphenylarsine obtained from the alcoholic solution weighed 2.4 g.; calcd. yield 3.1 g.; m. p. 59-60°.

Four and six-tenths grams of diphenylarsine (0.02 mole) dissolved in 10 cc. of alcohol, was mixed with 7.16 g. (0.02 mole) of the hydroxychloride, dissolved in 40 cc. of the same solvent. After twelve hours the solvent was removed, the diphenylchlaroarsine hydrolyzed to the corresponding oxide and the reaction products separated; yields. 2.7 g. of tetraphenylarsyl oxide, m. p. 90–92°, and 5 g. of triphenylarsine, mixed m. p. 59–61°.

Tetraphenyldiarsyl and Triphenylarsine Hydroxychloride (E).—Three and three-tenths grams of the isolated diarsyl, dissolved in 70 cc. of benzene, was mixed with 2.55 g. of the hydroxychloride, dissolved in 25 cc. of alcohol. After twenty-four hours the solvents were removed, the residue dissolved in petroleum ether and shaken with 5% sodium hydroxide solution, whereby the diphenylchloroarsine was converted into tetraphenylarsyl oxide. Upon concentration of the petroleum ether layer the oxide separated. Triphenylarsine was isolated from the mother liquor. Both products were recrystallized from alcohol. The yield of oxide, m. p. 91–94', was 1.7 g.; the yield of arsine, m. p. 59-61°, was 1.1 g.

Summary

The reactions which take place between phenylarsine and oxygen, sulfur, iodine and triphenylarsine dichloride, respectively, have been studied.

Interaction of diphenylarsine with each of the following substances has been investigated: oxygen, iodine tetraphenylarsyl oxide, tetraphenylarsyl sulfide, phenylchloroethoxyarsine, triphenylbromomethane, triphenylmethyl, triphenylarsine dichloride and triphenylarsine hydroxychloride.

In addition it has been shown that tetraphenyldiarsyl reacts with triphenylarsine dichloride and with triphenylarsine hydroxychloride.

ANN ARBOR, MICHIGAN

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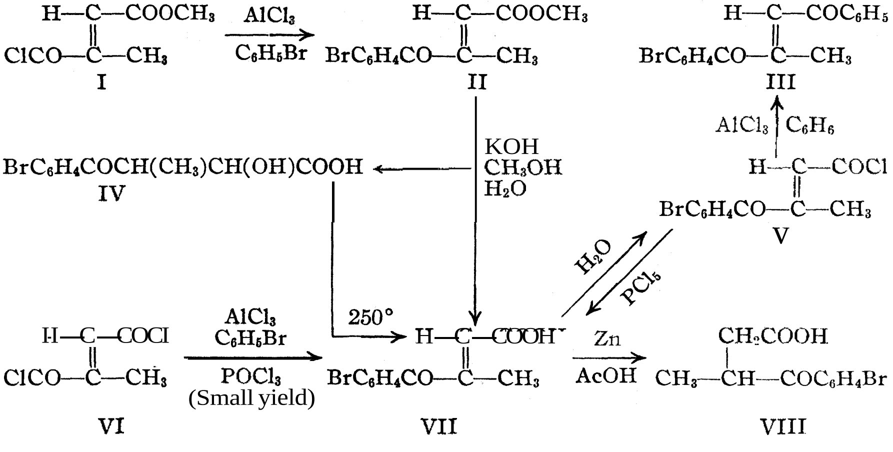
Studies on Unsaturated 1,4-Dicarbonyl Compounds. VII. Aryl Unsaturated 1,4-Diketones and Ketonic Acids Derived from Citraconic and Mesaconic Acids, with Particular Reference to the β-[p-Bromobenzoyl]-methylacrylic Acids

BY ROBERT E. LUTZ AND ROBERT J. TAYLOR

Two monomethyl unsaturated 1,4-ketonic acids have been described in the literature[1] but they have not been extensively studied and their configurations are not known. In an extension of our studies to this class of compounds we have utilized the bromophenyl analogs which are easily prepared, and have obtained three of the four possible isomers.

Trans-β-[*p*-Bromobenzoyl]-crotonic Acid (VII).—*Trans*-β-[*p*-bromobenzoyl]-crotonic methyl ester (II) was synthesized in good yield by the Friedel and Crafts reaction from mesaconyl a-methyl ester β-acid chloride (I), the structure of which is known.[2] From this synthesis the position of the methyl group is determined. The ester undergoes hydrolysis in dilute methanol to give two products, the expected trans acid (VII) (and also an addition compound, β-bromobenzoylhydroxybutyric acid (IV) which is described below). Under special conditions this trans acid is obtained also directly from mesaconyl chloride by the Friedel and Crafts reaction. The ester is easily regenerated.



The configuration of the acid and its derivatives must be trans, corresponding with that of the starting materials, since in Friedel and Crafts reactions of this type there is no reason to suppose that inversion in the

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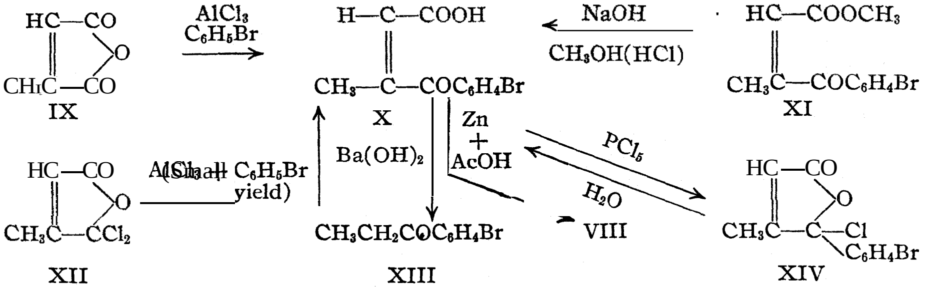
[1] (a) V. Pechmann, *Ber.*, 15, 891 (1882); (b) Bogert and Ritter, THIS JOURNAL, 46, 2871 (1924); 47, 526 (1925).

[2] Anschütz, Ann., 353, 139 (1907).

direction *trans* to *cis* is likely.[3] The acid chloride (V) reacts rapidly in the cold with methanol to form the ester and undergoes the Friedel and Crafts reaction with benzene and aluminum chloride to give the corresponding mixed diketone (III). It therefore reacts normally in contrast with the *cis* isomer described below. These facts are consistent with the *trans* formulation.

Cis-β-[*p*-Bromobenzoyl]-crotonic Acid (X).—The colorless *cis*-β-[bromobenzoyl]-crotonic acid (X) is prepared in a yield of 47% by the Friedel and Crafts reaction on citraconic anhydride with bromobenzene. It is obtained similarly from citraconyl chloride in a very small yield, but as the main product nevertheless.* It is a stereoisomer and not a structural isomer of the *trans* acid described above, since both acids are reduced to the same β-[bromobenzoyl]-butyric acid (VIII). It is easily esterified,[4a] and is regenerated in good yield from the ester by hydrolysis. The *cis* configuration follows from the synthesis since both stereoisomers are made, respectively, from starting materials of opposite and known configurations, and since no inversion from the one series into the other has been observed.

We have obtained independent proof of the position of the methyl group by the hydrolytic splitting of the *cis* acid at the double bond to give *p*-bromopropiophenone (XIII) which could only be formed if the methyl were alpha to the bromobenzoyl group. This degradation demonstrates that the Friedel and Crafts condensations occurred as expected para to the bromine in the benzene nucleus.



The acid chloride (XIV) of the *cis* isomer is easily prepared by the action of phosphorus pentachloride on the acid. It is a colorless solid which is hydrolyzed extremely slowly, and does not react readily with boiling methanol. The chlorine is therefore much less reactive than that of the

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[3] Lutz, THIS JOURNAL, 52, (a) 3405, (b) 3423 (1930).

[4] A relatively very minor yield of the *trans* structural isomer (XVI) was isolated as a by-product of the reactions with citraconic anhydride and chloride.

[4a] Since acceptance of this paper, Mr. A. W. Winne in this Laboratory has obtained the cis-β-[bromobenzol]-crotonic methyl esters in crystalline form (m. p. 62°, best prepared by alcoholysis of the acid chloride), and has obtained what appears to be an isomeric ester (m. p. 69°) by the silver salt method of esterification. These isomers correspond, we believe, to normal and cyclic types, and will be described in detail, together with analogs in the dimethyl and dihalogeno series in later papers.

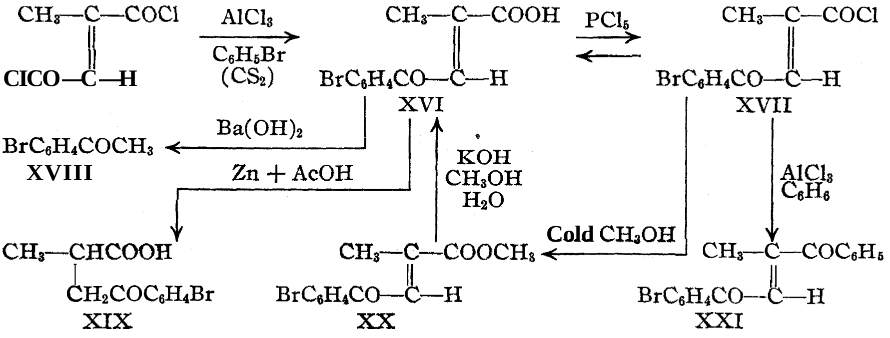
trans isomer. On the basis of these facts we have written the cis acid chloride as a γ-chlorocrotolactone. It is exactly analogous to *cis*-β-benzoyldibromoacrylyl chloride[Sa] (cf. also Ref. 4a).

The Friedel and Crafts reaction on the acid chloride gives a product in which, according to the analysis, chlorine has been replaced by bromophenyl. The product, however, is not a diketone, nor is it the expected γ,γ-di-[bromophenyl]-crotolactone, since it is an acid. We have not yet investigated its structure. It is clear, however, that the cis acid chloride has not reacted in a normal sense.

Trans-β-[p-bromobenzoyl1-a-methylacrylic Acid **(XVI)**.—We have obtained only one of the two possible structural isomers of the @-methyl acids (VII and X) described above, namely, *trans*-β-[bromobenzoyl]-α-methylacrylic acid (XVI). This acid is yellow and is the sole crystalline product obtained in a 60% yield by the Friedel and Crafts reaction on mesaconyl chloride.[4,5] The trans configuration follows from the synthesis.

Reduction yields a new acid which is isomeric with β-[bromobenzoyl]-butyric acid (VIII) and must therefore be β-[bromobenzoyl]-α-methylpropionic acid (XIX). Proof of the position of the methyl group and also that of the bromine atom was accomplished by the hydrolytic splitting of the parent trans acid (XVI) at the double bond to yield p-bromoacetophenone (XVIII).

The acid chloride, obtained by the action of phosphorus pentachloride, is a brilliant yellow solid which reacts rapidly with cold methanol to form the ester, is hydrolyzed rapidly in hot water, and reacts readily with benzene and aluminum chloride to give a mixed diketone (XXI) in good yield. It is therefore a normal acid chloride. These reactions are consistent with the trans formulation, and would not be expected of a cis isomer.



The Directing **Influence of the Methyl** Group.—The Friedel and Crafts reaction with citraconic anhydride proceeds in two senses structurally; it involves mainly the carbonyl adjacent to the methyl, and to a very minor

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(5) When the reaction is carried out in phosphorus oxychloride and bromobenzene, however, a 10% yield of the structural isomer (VII) is the only crystalline product isolated.

extent the other carbonyl (giving, respectively, X and XVI). Citraconyl chloride reacts similarly, but since the yields are very much smaller it is of course questionable whether or not the ratio of the two products (X and XVI) is a true measure of the two different reaction tendencies.

Mesaconyl chloride, in contrast with the cis isomer, reacts largely in the opposite sense[5] (to give XVI) involving the carbonyl chloride which is farthest removed from the methyl. A similar directing influence has been noted in the reaction with aromatic amines.[2]

Inversion from Cis to Trans during the Friedel and Crafts Reaction.—In the Friedel and Crafts reaction with bromobenzene and citraconic anhydride the methyl group on the ethylene linkage has stabilized the configuration since the principal product is a cis acid (X).[6] In the minor reaction involving the carbonyl to which the methyl is beta, complete inversion results (to give XVI). The expected fourth isomer, *cis*-β-[bromobenzoyl]-α-methylacrylic acid, has not been found and possibly is too labile to exist under the reaction conditions?

The governing factor in inversion during the reaction is clearly the position of the methyl group, or, as is probably more significant, the position of the mobile hydrogen atom with respect to the carbonyl group involved: in the reactions with maleic anhydride[3b] and in the minor reactions of citraconic anhydride and chloride, where hydrogen is alpha to the reacting carbonyl, inversion occurs; but when methyl is *alpha* as in the main course of the reaction with citraconic anhydride and bromobenzene (and also with dimethyl maleic anhydride and benzene),[8] no inversion occurs.

A Trans-trimethylbenzoylmethylacrylic Acid (XXII).—Mesitylene reacts with citraconic anhydride in the Friedel and Crafts reaction to give only one crystalline product in a 36% yield. This trimethylbenzoylmethylacrylic acid is brilliant yellow, a fact which indicates the trans configuration. Its acid chloride is unstable, but when treated cautiously in a Friedel and Crafts reaction with mesitylene, it gives a very small but significant yield of di-[2,4,6-trimethylbenzoyl]-methylethylene (XXIII), which is obtained also directly from mesaconyl chloride by the same reaction. Such a result is hardly to be expected of a cis acid chloride3 and may be regarded as evidence that the configuration is trans, and that inversion during the synthesis has taken place. The position of the methyl group has not been determined. It might be assigned on the basis of the observation noted above that inversion during the preparation of the bromobenzoyl analog occurs only when hydrogen is alpha to the carbonyl involved in the reaction; but on the other hand bromobenzene reacts largely in the opposite sense structurally; furthermore, in the

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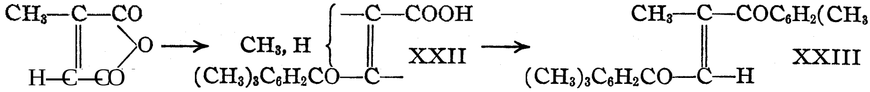
(6) In the analogous preparation of aroylacrylic adds from maleic anhydride, inversion is complete.[3b]

(7) Cf. the unknown *cis*-β-benzoylacrylic acid (Ref. 3b).

(8) Lutz and Taylor, ninth paper of this series, to be published later.

analogous reaction with dimethylmaleic anhydride and mesitylene inversion has apparently occurred where no alpha hydrogen exists.[8]



β-[Bromobenzoyl]-α(?)-hydroxybutyric Acid (IV).—In the hydrolysis of β-[bromobenzoyl]-crotonic methyl ester (11), a side reaction takes place involving the addition of the elements of water, probably by a 1,4-addition followed by hydrolysis, to give β-[bromobenzoyl]-α(?)-hydroxybutyric acid (IV). The greater the percentage of water in the hydrolytic solvent, the better the yield of the expected trans acid, whereas in nearly absolute methanol no trans acid was isolated. The nature of this addition compound was shown by pyrolysis, water being eliminated to give trans β-bromobenzoylcrotonic acid (VII). The position of the hydroxyl group is undoubtedly alpha to the carboxyl, since addition to the more active conjugated system, favored also by the steric hindrance of the methyl group, would be expected. β-Benzoylacrylic methyl ester reacts in this sense during hydrolysis.[9] Addition compounds of this type were not isolated in the hydrolysis of either the cis ester or the structurally isomeric trans ester, but were probably present in the oily by-products of these reactions.

Methyl Unsaturated 1,4-Diketones.[10]—The trans methyl unsaturated 1,4-diketones were prepared from mesaconyl chloride by the Friedel and Crafts reaction. Bromobenzene, however, failed to give a diketone in an analogous experiment, mesaconyl chloride reacting only part way under a variety of conditions to give the intermediate *trans*-β-[bromobenzoyl]-methylacrylic acids. The acid chlorides of these latter substances appear to give only complex resinous products when the Friedel and Crafts reaction with bromobenzene is forced under more drastic conditions; yet benzene reacts readily enough in both cases to give the corresponding mixed diketones, III and XXI. This failure of bromobenzene to react in the second stage of the Friedel and Crafts reaction is surprising since the analogous reaction with fumaryl chloride gives the corresponding diketone in excellent yield.[11]

The configurations of the diketones follow from the synthesis.[3] Trans dibenzoylmethylethylene (XXIV) on exposure to the sunlight in a solvent gives the cis isomer in a fair yield, apparently irreversibly, together with resinous decomposition products. Both stereoisomers are reduced to the same 1,2-dibenzoylpropane (XXVI).

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(9) Rice, THIS JOURNAL, 46, 222 (1923).

(10) The preparation of the diketones from mesaconyl chloride was first carried out by Mr. W. W. Huang under the direction of the senior author, in the Nichols Chemical Laboratory of New York University. We have repeated and extended this work.

(11) Conant and Lutz, THIS JOURNAL, 47, 881 (1925)

$$C_6H_5COCH{=}C(CH_3)COC_6H_5 \xrightarrow{Zn\ +\ AcOH} C_6H_5COCH_2CH(CH_3)COC_6H_5$$

$$\textit{Trans}\ \text{XXIV} \xrightarrow{\text{Sunlight}} \textit{Cis}\ \text{XXV} \qquad\qquad \text{XXVI}$$

The *cis* isomer could not be rearranged back to the *trans* by the action of iodine and sunlight. Overlong exposure to the sunlight converts either form into intractable oils, and it is possible that the transformation cis to *trans* does occur, but that the *trans* isomer is the more easily resinified by the action of sunlight and is destroyed as fast as it is formed. It is obvious in any case that the *cis* isomer results from the *trans* by the absorption of light energy, and although not rearranged back is nevertheless to be regarded as potentially the labile form with the higher energy content.

The Effect of the Methyl Group on Color.—The unsubstituted *trans* aryl unsaturated 1,4-diketones and ketonic acids are all to some degree yellow, and the cis isomers colorless. The aroyl group is undoubtedly responsible for the shift of absorption into the visible region, fumaric acid types being colorless. The color is diminished if not destroyed by ethylenic substituents such as halogen and aroxyl. The methyl group in the diketone series diminished the color very markedly. Of the two *trans* p-[bromobenzoyl]-methylacrylic acids, the one in which the methyl is adjacent to the aroyl group (VII) is almost colorless, the other (XVI) is bright yellow.

Experimental Part

Citraconic and Mesaconic Acids

The conversion of citraconic to mesaconic acid[12] by the action of sunlight on a chloroform–ether solution containing bromine proceeds best in large scale runs on 700 g. of material to give yields as high as 85%.

Mesaconyl chloride was prepared according to Petri.[13] In one large scale preparation from 650 g. of acid the fractionation at atmospheric pressure involved long heating of the bulk of the material. An end fraction of 82 g. of pure citraconyl chloride was collected and identified by its boiling point (96–97° corr. at 15 mm.), and by nearly quantitative hydrolysis to citraconic acid (no mesaconic acid being detected). Similar results were obtained when mesaconyl chloride was refluxed for three hours or was heated at 100° with 20% of its weight of aluminum chloride, but when allowed to stand in diffused light for one year, or heated for one hour at 50° (the conditions of the average Friedel and Crafts reaction) no such inversion was detected.

A sample of mesaconyl chloride was hydrolyzed completely upon standing twenty-four hours with water. In a similar experiment citraconyl chloride was not completely hydrolyzed until about five days had elapsed. We regard this abnormally slow hydrolysis in the latter case as possible evidence in favor of the cyclic formulation (XII).

Partial alcoholysis of mesaconyl chloride with one equivalent of methanol gave a mixture consisting largely of unchanged material and dimethyl ester.

Mesaconyl a-methyl acid ester was prepared by the method of Anschütz,[2] but longer standing (fifty hours) gave a better yield (74%); b. p. 122° (corr.) under 4 mm.

Dimethyl ester,[2] b. p. 99.5° (corr.) at 18 mm.

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[12] Fittig and Landolt, Ann., 188, 72 (1877). See also Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," 1931, pp. 243, 406, 414.

[13] Petri, *Ber.*, 14, 1635 (1881).

Aryl α,β-Unsaturated 1,4-Ketonic Acids

Trans-β-[*p*-bromobenzoyl]-crotonic Acid (VII).—The methyl ester (4 g.) was dissolved in 30 cc. of hot methanol and the mixture chilled to give a mass of fine crystals: 15 cc. of water containing 1.2 g. of potassium hydroxide was then added, and the mixture shaken (machine) until complete solution took place (about twenty minutes). The mixture was diluted with water and extracted with ether from which a small amount of unchanged ester was recovered. The aqueous solution was acidified and the product extracted into ether and isolated on subsequent evaporation as an oil. This gave a total of 1.9 g. (50%) of nearly pure crystalline *trans* acid from a benzene–ligroin mixture. The filtrate yielded the addition product (see below); crystallized as thin rectangular scales from benzene; m. p. 144.5–145° (corr.).

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.37. Found: C, 49.07; H, 3.72.

Several attempts were made to prepare the corresponding diketone from mesaconyl chloride with two equivalents of phosphorus oxychloride, bromobenzene, and aluminum chloride, heating the mixture on a steam-bath for five minutes. Small yields (5–10% in several runs) of the above acid were isolated and identified.

A small sample was reduced with zinc and acetic acid in the usual way, and a small yield of β-[bromobenzoyl]-butyric acid was isolated and identified by a mixed melting point.

β-[*p*-Bromobenzoyl]-α(?)-hydroxybutyric Acid (IV).—The benzene–ligroin mother liquor from the above preparation was evaporated to an oil which began to crystallize on standing several days. It was taken up again in benzene and ligroin, cooled and filtered to give 0.9 g. (22%) of nearly pure material; crystallized as thin hexagonal or boat-shaped scales from benzene–ligroin mixtures: m. p. 85–86° (corr.); soln. in sodium bicarbonate.

Anal. Calcd. for $C_{11}H_{11}O_4Br$: C, 45.99; H, 3.86. Found: C, 46.14; H, 4.42.

A small sample of the above acid was heated quickly to 250" in an oil-bath and allowed to cool. As the temperature reached 150° the molten product boiled and moisture condensed in the delivery tube. The orange colored oily residue was dissolved in benzene, ligroin was added, and on seeding a good yield of trans-bromobenzoylcrotonic acid crystallized and was identified by mixed m. p. with known material.

Trans β-[*p*-Bromobenzoyl]-crotonic Methyl Ester (II).—Ten grams of mesaconyl α-methyl acid ester was allowed to react with 16 g. of phosphorus pentachloride. The liquid mixture containing two equivalents of phosphorus oxychloride was filtered from a small amount of unchanged phosphorus pentachloride, rinsing with carbon disulfide. This solution was then added slowly to a well-stirred mixture of 20 g. of bromobenzene and 60 g. of aluminum chloride in 100 cc. of carbon disulfide. The reaction mixture was refluxed for two hours and decomposed in the usual way. The carbon disulfide solution was evaporated. The oily residue partly crystallized on standing, and was diluted with petroleum ether and filtered; yield of nearly pure product, 11.5 g. (66%); crystallized as almost colorless (yellowish tinted), long, thin rectangular scales from alcohol; m. p. 75.5° (corr.). It dissolves to give a deeply yellow solution. It gives a sharp mixed melting point depression with the isomeric a-methylacrylic ester.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 51.07; H, 4.08.

Hydrolysis in dilute methanolic potassium hydroxide gave mixtures of the acid and the addition product, bromobenzoyl-a-hydroxybutyric acid. The latter was the sole product isolated when pure methanol (without added water) was used as the solvent. The yield, however, was not good.

Trans-β-[*p*-bromobenzoyl]-crotonyl Chloride (V).—Obtained as a yellow oil by the action of phosphorus pentachloride on the acid, with vacuum desiccation to remove phosphorus oxychloride. A droplet was hydrolyzed to the acid when heated for two minutes with water. It reacted rapidly in the cold with methanol, the ester crystallizing quickly from the solution. A separate Friedel and Crafts reaction with bromobenzene was not carried out directly on this acid chloride, but β-[bromobenzoyl]-crotonic acid was isolated from typical reactions between mesaconyl chloride, bromobenzene, and aluminum chloride, in which the crotonyl chloride was undoubtedly present as an intermediate under conditions which would normally have led to the formation of the diketone.

Cis-β-[*p*-bromobenzoyl]-crotonic Acid (X).—Citraconic anhydride (50 g.) was added slowly over a period of one hour to a well stirred mixture of 134 g. of finely ground aluminum chioride in 140 g. of bromobenzene and 100 cc. of carbon disulfide, the reaction mixture being kept at 50°, subsequently heated for half an hour, and allowed to stand overnight. It was decomposed in ice and hydrochloric acid. Upon separating and evaporating the carbon disulfide layer the crude product crystallized; yield, nearly pure 57.2 g. (47%); cryst. as colorless, square or octahedral prisms, m. p 142.5" (corr.).

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.37. Found: C, 49.35; H, 3.47.

From the oily residues of the above experiment a crystalline product was isolated recrystallized from chloroform, and identified as *trans*-β-[bromobenzoyl]-α-methylacrylic acid; yield 2 g. (2%).

When 10 g. of citraconyl chloride was used in a Friedel and Crafts reaction under approximately the same conditions as above, a total of 2 g. (12.5%) of the above described cis acid (X) was isolated, together with a very small amount (0.05 g.) of the trans-a-methylacrylic acid (XVI). It is very unlikely that this a-methyl isomer came from mesaconyl chloride present as an impurity in the starting material. The sample of acid chloride used gave only citraconic acid on hydrolysis.

A benzene solution of the cis acid with aluminum chloride was heated on the steam-bath for one hour. Only unchanged material was recovered.

A suspension of 3 g. of the cis acid in water with 10 g. of barium hydroxide was distilled, and the steam distillate (0.5 g.) of m. p. 43–44° (corr.) was identified as *p*-bromobenzophenone by a mixed melting point with a known sample.

Cis-β-[*p*-bromobenzoyl]-crotonic Methyl Ester (XI).—The ester was prepared by allowing the acid to stand for one week in saturated methanolic hydrochloric acid. It was isolated by decomposing the mixture in iced sodium carbonate solution, extracting into ether, drying with anhydrous sodium carbonate. and distilling under reduced pressure; yield 4.1 g. (78%); colorless oil of b. p. 156–158° at 4 mm.

Anal. Calcd. for $C_{12}H_{11}O_3Br$; C, 50.88; H, 3.92. Found: C, 50.79; H, 4.15.

Hydrolysis of 1 g. by allowing it to stand for twenty-four hours in 10 cc. of 95% ethanol containing 0.1 g. of dissolved sodium, gave a yellow oil from which 0.82 g. of crude cis acid crystallized and was identified.

Cis-γ-[*p*-bromophenyl]-γ-chloro-β-methyl Crofolactone **(Cis-(ψ)β-[*p*-bromobenzoyl]-crotonyl** Chloride) **(XIV).**—The acid (2 g.) was allowed to react with 1.56 g. of phosphorus pentachloride, the mixture being warmed gently to start the reaction. The acid chloride crystallized from the phosphorus oxychloride solution and was filtered; yield 1.96 g. (91%); colorless; crystallized from benzene; m. p. 82.5° (corr.).

Anal. Calcd. for $C_{11}H_8O_2BrCl$: C, 45.92; H, 2.81. Found: C, 45.89; H, 2.91.

A small sample required one week, standing in contact with water to undergo complete hydrolysis. The reaction was quantitative. The acid chloride dissolves in hot alcohol and crystallizes on cooling unchanged.

The Friedel and Crafts reaction in a number of experiments under a variety of conditions gave only one product. In a typical experiment on 1.4 g. of the acid chloride, 1.38 g. (69%) of a colorless solid was isolated; crystallized from bromobenzene; m. p.

208° (corr.). It is soluble in cold dilute sodium carbonate with effervescence, and is precipitated crystalline by acids and by an excess of sodium ion.

Anal. Calcd. for $C_{17}H_{12}O_2Br_2$: C, 50.01; H, 2.96; Br, 39.18. Found: C, 50.06; H, 3.00; Br, 39.39, 39.54.

β-[*p*-Bromobenzoyl]-butyric Acid (VIII).—The above *cis* acid (2 g.) was reduced with zinc and boiling acetic acid in the usual way; yield 1.35 g. of pure product; crystallized from chloroform and petroleum ether; m. p. 95.5° (corr.).

Anal. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.71; H, 4.09. Found: C, 48.39; H, 4.18.

Trans-β-[*p*-bromobenzoyl]-α-methylacrylic Acid (XVI).—Mesaconyl chloride (25 g.) was added slowly to a well-stirred mixture of 70 g. of bromobenzene and 45 g. of aluminum chloride, heated on a steam-bath. Upon decomposing in ice and concentrating the carbon disulfide layer, 25 g. of crude product (60%) was isolated;[14] crystallized as yellow needles from chloroform or benzene; m. p. 188° (corr.).

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.37. Found: C, 49.03, 49.16; H, 3.45, 3.47.

Steam distillation of a suspension of the acid in water with barium hydroxide gave p-bromopropiophenone which was identified by a mixed melting point with a known sample prepared from propionyl chloride and bromobenzene, and by the characteristic melting point of its oxime.

Trans-β-[*p*-bromobenzoyl]-α-methylacrylic Methyl Ester (XX).—Prepared by the interaction of the acid chloride and methanol; crystallized from ethanol as long, thin, square-ended needles of a very pale yellowish color; m. p 86° (corr.). A mixed melting point with the stereoisomer showed a sharp depression.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 51.18; H, 4.05.

Hydrolysis of 0.11 g. of the ester with potassium hydroxide in 80% methanol gave 0.03 g. of pure acid. This is to be regarded as a fair yield since difficulty in handling the sample resulted in some losses.

Trans-β-[*p*-bromobenzoyl]-α-methylacrylyl Chloride (XVII).—The acid (3 g.) reacted with 3 g. of phosphorus pentachloride to give an oil which crystallized. On diluting with petroleum ether, cooling and filtering, 2.2 g. was isolated; crystallized from ligroin as brilliant yellow, thin, diamond-shaped plates of m. p. 66° (corr.), turning bright red at 100 to 150°. On standing for two days the solid was transformed into a brown resinous mass with the evolution of considerable hydrogen chloride.

Anal. Calcd. for $C_{11}H_8O_2ClBr$: C, 45.92; H, 2.81. Found: C, 45.77; H, 2.99.

A small sample was hydrolyzed completely when heated for ten minutes with water in a steam-bath. It dissolved quickly in cold methanol, and almost immediately the ester crystallized and was filtered off and identified by a mixed melting point. In a typical Friedel and Crafts reaction in bromobenzene at 70–80° the *trans* acid was recovered, but no other crystalline product was found.

β-[*p*-Bromobenzoyl]-α-methylpropionic Acid (XIX).—The *trans* acid (1 g.) was reduced by zinc and acetic acid in the usual way, and gave 0.8 g (80%) of nearly pure product; crystallized from benzene; m. p. 124° (corr.); colorless.

Anal. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.71; H, 4.09. Found: C, 49.09; H, 4.08.

Trans-β-[2,4,6-trimethylbenzoyl]-methylacrylic Acid (XXII).—Prepared by a typical Friedel and Crafts reaction on citraconic anhydride with mesitylene in carbon disulfide, but with short heating (ten minutes) to minimize resinification. The product was isolated by steam distillation to remove mesitylene and carbon disulfide, and crys-

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[14] From the mother liquors a small amount of a colorless solid (not an acid) of m. p. 140.5° (corr.) was isolated. It crystallizes from benzene and has not yet been identified.

tallizing the oily residue from benzene–petroleum ether mixtures. From 10 g. of anhydride, a total of 7.4 g. (36%) of crude product was obtained, the rest of the material going into intractable oils; bright yellow crystals from benzene. m. p. 142° (corr.).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.37; H, 6.95. Found: C, 72.53; H, 6.87.

The acid gave an unstable oily acid chloride which decomposed when purification was attempted. On standing with water it was hydrolyzed back to the *trans* acid. The Friedel and Crafts reaction under ordinary conditions gave only resinous products, but when the reaction was controlled and allowed to run for only one minute a small yield of crystals (0.075 g. from 0.5 g. of the acid) was isolated and identified by a mixed melting point as trimethylbenzoylmethylethylene. The large amounts of oily by-products interfere seriously with the isolation of the product.

Trans-β-[2,4,6-trimethylbenzoyl]-methylacrylic Methyl Ester.—Prepared by the action of saturated methanolic hydrogen chloride on the acid (standing for one week), and isolated in the usual way; yield **4.5** g. from 5 g. of acid (85%); yellow oil; b. p. 144.5" (corr.) at 5 mm.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.13; H, 2.37. Found: C, 72.82; H, 7.42.

The Diaroyl Methylethylenes[10]

Trans-1,2-dibenzoylpropene-1 (Dibenzoylmethylethylene) (XXIV).—Mesaconyl chloride (25 g.) was added dropwise to a well-stirred mixture of aluminum chloride in 45 g. of benzene and 50 cc. of carbon disulfide over a period of twenty minutes. The red reaction mixture was then stirred at room temperature for two hours, heated for ten minutes, and decomposed in ice and hydrochloric acid. The carbon disulfide solution was dried over sodium sulfate and upon concentrating and cooling gave 27 g. of crude crystalline diietone (72%); crystallized from benzene or alcohol; very pale yellow; m. p. 52° (corr.).

A d . Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.27; H, 5.70.

The diketone reacts with bromine under a variety of conditions but gives largely oils, with the evolution of hydrogen bromide and the formation of lachrymatory by-products. Bromination in chloroform at boiling temperature, however, gave a product which crystallized from chloroform and petroleum ether; m. p. 130° (corr.).

Cis-1,2-dibenzoylpropene-1 *(Dibenzoylmethylethylene)* **(XXV).**—The *trans* isomer (5 g.) in 25 cc. of alcohol was exposed to direct sunlight for four days. The solution upon concentrating and cooling gave 3 g. of colorless crystals of the *cis* isomer (yield 60%). Resinous by-products remained in solution; colorless needles; cryst. from alcohol; m. p. 68.5' (corr.).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.54; H, 5.58.

Solutions of the *cis* isomer in alcohol, chloroform and benzene, containing a tract of iodine, were exposed to direct sunlight for lengths of time varying between five hours and two days. Only unchanged material and resinous by-products were isolated.

One gram of the *cis* isomer was reduced with zinc and acetic acid to give 0.9 g. (89%) of 1,2-dibenzoylpropane.

1,2-Dibenzoylpropane (XXVI).—*Trans*-dibenzoylmethylethylene (5 g.) in 150 cc. of hot acetic acid was treated with 20 g. of zinc dust and the mixture boiled for fifteen minutes. Upon filtering, cooling and diluting with water, an oily product separated which soon crystallized; yield of crude product, 4.1 g. (81%); crystallized from alcohol; colorless; m. p. 105° (corr.).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 80.76; H, 6.32.

Trans-1,2-di-[2,4,6-trimethylbenzoyl]-propene-1 $(CH_3)_3C_6H_2COC(CH_3){=}CHCO{-}C_6H_2(CH_3)_3$.—Mesaconyl chloride (50 g.) was added to a well-stirred mixture of 80 g.

of aluminum chloride in 75 g. of mesitylene and 200 cc. of carbon disulfide, and the red reaction mixture heated for fifteen minutes. The nearly pure diketone was isolated in the usual way; yield 68 g. (68%); crystallized from alcohol; yellow; m. p. 96° (corr.).

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 82.58; H, 7.84. Found: C, 82.27; H, 7.96.

A number of attempts under a variety of conditions to prepare the *cis* isomer from the *trans* by exposure of the latter to sunlight failed, either unchanged material or intractable oils being obtained. Reduction under a variety of conditions failed to give a crystalline product.

Bromination under a variety of conditions gave largely non-crystalline products, and hydrogen bromide was liberated. Bromination at 0° in chloroform gave a mixture of products from which two substances were isolated. Analysis indicated one of these (m. p. 176°) to be a *dibromide*, and the other (m. p. 134°) a *monobromoethylene*.

Trans-1-benzoyl-2-bromobenzoylpropene-1 (III).—*Trans*-bromobenzoylcrotonyl chloride from 0.5 g. of the acid and 0.5 g of phosphorus pentachloride was treated directly (without separating from phosphorus oxychloride) with 3 cc. of benzene and 3 g. of aluminum chloride. A deep red solution formed. After standing for four minutes the mixture was decomposed in ice and the benzene layer separated, extracted with sodium carbonate, dried and evaporated to yield an oil which crystallized from alcohol; yield 0.35 g. (59%); crystallized from ethanol as pale yellow, thin, elongated, rectangular leaflets; m. p. 73–74° (corr.). It is yellow in solution.

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.00; H, 3.97. Found: C, 62.30, 62 27; H, 4.13, 4.07.

Trans-1-bromobenzoyl-2-benzoylpropene-1 (XXI).—Prepared in exactly the same way as the above isomer; yield 0.85 g. (72%) from 1 g. of the acid; crystallized from ethanol as pale cream-tinted, almost colorless, thin, diamond-shaped leaflets; m. p. 56° (corr.).

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.00; H, 3.97. Found: C, 62.20; H, 3.95.

Summary

Cis and *trans* β-bromobenzoylcrotonic acids and *trans*-β-[bromobenzoyl]-α-methylacrylic acid, and a number of derivatives, have been prepared and their structures and configurations elucidated. The effect of the substituted methyl group in the various reactions concerned is discussed.

The synthesis of methyl unsaturated 1,4-diketones is described.

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The Reaction of Aromatic Ketones with Sodium. I. The Structure of the So-called Metal Ketyls

BY W. E. BACHMANN

Beckmann and Paul[1] observed that aromatic ketones react with metallic sodium in anhydrous ether and give deeply colored sodium derivatives; they considered that the compounds were dimolecular and had the formula $(R_2)NaC—O—CONa(R_2)$. Twenty years later, Schlenk[2] and co-workers took up the study of these compounds. The intense colors of the compounds and the reactions with iodine and with oxygen indicated to them the presence of a radical analogous to the triarylmethyls and they came to the conclusion that the sodium compounds are free radicals of the type, R_2CONa, formed by addition of an atom of sodium to a molecule of ketone. According to Schlenk, these ketyls, as they were named, are monomolecular and do not associate to the dimolecular form, sodium pinacolate, $R_2C(ONa)(NaO)CR_2$. The strongest support for the monomolecular structure has been the observation of Schlenk and co-workers that hydrolysis of the compounds does not give pinacols but always a mixture of ketone and hydrol. They rightly remark that if the sodium derivative had the dimolecular structure of sodium pinacolate, then pinacols should result on hydrolysis; and it is noteworthy that in not a single instance did Schlenk obtain a pinacol. According to him the formation of ketone and hydrol can be explained only on the basis of ketyl radicals and they formulated the reaction as follows

$$2R_2C—ONa \xrightarrow{H_2O} 2R_2C—OH \longrightarrow R_2CO + R_2CHOH \qquad (1)$$

Schlenk's views regarding the structure of the ketone–sodium compounds have been generally accepted[3] or at least uncontested.[4] That these views are held at the present time is evident from the recent statements of Bergmann;[5] according to him "the ketyls are practically monomolecular" and "it is impossible to obtain pinacols from the sodio-ketyls." For the past twenty years it has been considered that the sodium derivatives are free radicals existing in the monomolecular state.

In 1927 it was shown with Professor M. Gomberg[6] that aromatic ketones react with a mixture of magnesium and magnesium iodide and are reduced

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(1) Beckmann and Paul, Ann., 266, 6 (1891).

(2) Schlenk and Weickel, Ber., 44, 1183 (1911); Schlenk and Thal, ibid., 46, 2840 (1913); Schlenk, Appenrodt, Michael and Thal, ibid., 47, 486 (1914).

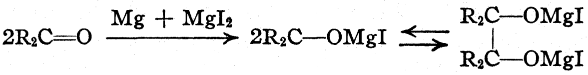
(3) See for example the articles on metal ketyls in Stewart's "Recent Advances in Organic Chemistry," London, 1932, Vol. II, p. 335; and in Walden's "Chemie der freien Radikalen," Leipzig, 1924, p. 100.

(4) Schmidlin's view ["Das Triphenylmethyl," Stuttgart, 1914, pp. 186–1881 that the compounds are loose combinations of the type, $R_2C{=}O\ldots Na$, has been shown to be incorrect, at least in liquid ammonia. Wooster, THIS JOURNAL, 51, 1856 (1929).

(5) Bergmann, *ibid.*, 54, 3773 (1932).

(6) Gomberg and Bachmann, *ibid.*, 49, 236 (1927).

to iodomagnesium pinacolates, $R_2C(OMgI)(IMgO)CR_2$. Although colorless in the solid state, these pinacolates give colored solutions; this fact led us to the conclusion that in solution the pinacolates dissociate to a slight extent into iodomagnesium-ketyl radicals, R_2C—OMgI, and this hypothesis was confirmed by the reactions of the solutions with iodine and with oxygen in the manner of the corresponding sodium compounds. The reduction of the ketones by the mixture of magnesium and magnesium iodide was, therefore, interpreted as taking place in the following manner



$$2R_2C{=}O \xrightarrow{Mg + MgI_2} 2R_2C{-}OMgI \rightleftarrows \begin{array}{c} R_2C{-}OMgI \\ | \\ R_2C{-}OMgI \end{array} \qquad (2)$$

That the latter equilibrium between the iodomagnesium-ketyl and the iodomagnesium pinacolate is nearly entirely (>99%) in favor of the pinacolate is shown by the fact that hydrolysis of the mixture gives nearly quantitative yields of pinacol and none of the mixture of ketone and hydrol.

Because of the similarities between the iodomagnesium derivatives and the sodium compounds in the matter of color formation and reaction with iodine and with oxygen, it has seemed incredible that an enormous difference exists between the two in the matter of structure. It seems impossible that the sodium pinacolates dissociate practically 100% to ketyl radicals, as is indicated by lack of pinacol formation, while the iodomagnesium pinacolates break down less than 1%, as shown by the yields of pinacol. In spite of the statements that pinacols are never formed on hydrolysis of the sodium compounds, we turned to this reaction in order to determine whether the sodium derivatives are actually monomolecular.[7] We followed the directions of Schlenk and co-workers and carried out about a dozen experiments with benzophenone and a number of other ketones. The colored mixtures which were obtained by the action of sodium on the ketones were hydrolyzed in an inert atmosphere either by pouring the mixtures into water or by adding alcohol to the mixture, a method frequently employed by Schlenk to replace the sodium by hydrogen, especially when using the apparatus recommended by him.[8] In every case a careful search failed to reveal even a trace of pinacol; the products consisted of mixtures of ketone and hydrol in agreement with Schlenk.

The clue to the solution of the problem was furnished by an observation, made during the investigation, that a small amount of alkali can rapidly effect the decomposition of a large amount of pinacol into a mixture of ketone and hydrol.[9] It occurred to us that pinacol is formed on hydrolysis

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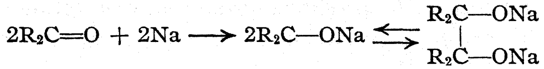
(7) We agree with Bergmann that the free ketyl itself would not give pinacol but ketone and hydrol on hydrolysis; if pinacol is formed it must come from sodium pinacolate. Although Schlenk mentioned that there might be ketones which would give pinacolates or mixtures of pinacolates and ketyls, he apparently never found such conditions in any case studied by him.

(8) See Schlenk and Thal, Ref. 2, for apparatus and methods of preparing and handling the metal ketyls.

(9) Bachmann, THIS JOURNAL, 66, 355 (1933); see also *ibid.*, 66, 770 (1933) for an application of the reaction.

of the ketone–sodium compounds and that the pinacol is subsequently broken down into ketone and hydrol by the action of the alkali liberated simultaneously on hydrolysis. It was thought that if the formation of alkali could be prevented, then pinacol would be obtained. With this thought in mind the mixtures were hydrolyzed by pouring them with vigorous stirring into dilute acetic acid. The results of the experiments fully substantiated the correctness of our idea. Hydrolysis with acetic acid gave pinacols in yields as high as 95%; practically no hydrol was formed. According to our theory it should be possible to get a quantitative yield of a pinacol that is not affected by alkali. Such a pinacol is 9,10-diphenyldihydrophenanthrenediol, and in confirmation of our theory it was found that this pinacol is obtained in 100% yield. These results show that the reaction between ketones and sodium proceeds in the following manner



$$2R_2C{=}O + 2Na \longrightarrow 2R_2C{-}ONa \rightleftarrows \begin{array}{l} R_2C{-}ONa \\ \;| \\ R_2C{-}ONa \end{array}$$

From this it follows that *the sodium derivatives of ketones, the so-called metal ketyls, are not monomolecular free radicals but sodium pinacolates or equilibrium mixtures of sodium-ketyl and sodium pinacolate in which the equilibrium is nearly entirely in favor of the sodium pinacolate* (Equation 3).

It is now easy to see why Schlenk, Bergmann and others have been misled in interpreting the reactions and the structures as they did. If the reaction mixture is decolorized by adding alcohol, there is no chance for the pinacol to survive; as soon as it is formed it is converted to a mixture of ketone and hydrol by the action of the sodium alcoholate, a reaction that is remarkably rapid. In a similar manner, if the mixture is poured into water the alkali which is formed will decompose the pinacol. Since the ketone and hydrol are products of a secondary reaction, the conclusions that have been drawn in the past from their presence cannot be correct.

Comparison of Metal **Pinacolates.**—It was found that of the metals of the first group lithium, potassium, rubidium and cesium give colored derivatives of benzophenone which give benzopinacol on hydrolysis. Of the second group metals, beryllium (with beryllium iodide),[6] magnesium (with magnesium iodide or as amalgam) and calcium likewise react with benzophenone and give colored derivatives. The actions of these metals on benzophenone and the products that are formed are similar. In each case colors are produced in the reaction; if the color is that of the ketyl, then the various metal ketyls of the formula $(C_6H_5)_2C{-}OMe$, where Me is the group indicated, have the following colors: Li, blue; Na, blue; K, violet-blue; Rb, blue; Cs, blue; IBe, red; Mg/2, blue; IMg, red; Ca/2, green. In every instance it is considered that the ketyls are intermediate products and that they associate nearly completely to the metal pinacolates, so that an equilibrium mixture of the two is formed. The amount of dissociation of the pinacolate varies with the pinacolate; in no case is the dissociation great. All of the pinacolates react with iodine and with oxygen and give back the ketone in virtue of the slight dissociation of the pinacolates into the ketyl radicals; the individual ketyls may vary considerably in their reactivity with various reagents. If the pinacol is not decomposed by the alcoholate or hydroxide of the metal, no special precautions, except protection from oxygen, need be taken with regard to the manner of carrying out the hydrolysis; the chief reason why quantitative yields of pinacols are easily obtained from the iodomagnesium pinacolates is the fact that the pinacols are not affected by iodomagnesium hydroxide or alcoholate. Although the reaction of ketones with sodium may be employed as a method of preparing pinacols, it is hardly likely that the reaction will be used in place of the $Mg + MgI_2$ reaction because the latter method has so many advantages. It is clear that there are no real differences in the structures of the products obtained from ketones and different metals; there is simply a gradation of properties in the series of metal pinacolates that are formed.

Experimental

In all experiments moisture and air were rigorously excluded. All operations were carried out in a stream of nitrogen which was purified by being passed through concentrated sulfuric acid and through a solution of benzophenone-disodium. The latter reagent is able to react with oxygen, water and carbon dioxide and is, therefore, a convenient purifying agent. The mixture was prepared by shaking a solution of 5 g. of benzophenone in 50 cc. of ether and 50 cc. of toluene in a wash-bottle with 5 g. of 40% sodium amalgam until the mixture was violet-red in color; this reaction required several days.

The reactions were usually carried out in glass-stoppered graduated cylinders; the glass stopper was sealed with the new lubricant of Meloche and Fredrick,[10] the top was covered with paraffin and the stopper was tied down; the flask was shaken mechanically. In many experiments 2% sodium amalgam was used in place of the metal alone; the mercury prevents to a great extent the formation of the disodium derivative,[11] except in the case of fluorenone. Hydrolysis was carried out by forcing the mixture by a stream of nitrogen into 400 cc. of 10% acetic acid (freshly boiled) contained in a I-liter, 3-necked flask which was fitted with an inlet tube, an outlet tube passing through a mercury trap and a mercury-sealed stirrer. The mixture is run into the acid slowly in order to avoid accumulation of the sodium compound, for it too can decompose the pinacol. One must constantly bear in mind that the decomposition of the pinacol by alkali is extremely rapid; only after dozens of experiments were carried out was it possible to obtain consistently high yields of pinacols. Best results were obtained if the ketone was not converted completely to the sodium derivative; excess of either ketone or metal was isolated at the end of the reaction and taken into account in calculating the yield of product. At times considerable amounts of ketone were obtained even when a sufficient amount of sodium had apparently reacted.

Reaction of Benzophenone with Sodium.—Five to ten gram portions of benzophenone in 120 cc. of ether were shaken with 100 g. of 2% sodium amalgam. The solution quickly became green and then dark blue; after several days a large amount of pale blue precipitate was present. The mixtures were hydrolyzed after being shaken for

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(10) Meloche and Fredrick, THIS JOURNAL, 54, 3264 (1932).

(11) Schlenk and Bergmann, Ann., 464, 26 (1928).

periods of time ranging from two days to two months. The ether solutions were separated from the aqueous solution, dried, filtered and evaporated. The benzopinacol obtained in this manner was stirred with 20 cc. of 80% alcohol in order to remove benzohydrol,[12] if any were present, and after filtration the pinacol was warmed with 20 cc. of petroleum ether (60–90°) in order to remove benzophenone, The pinacol was then recrystallized from a mixture of chloroform and alcohol. From the alcohol and petroleum ether extracts small amounts of pinacol were isolated. In an experiment in which 7.5 g. of benzophenone had reacted during two weeks of shaking there was obtained 6.5 g. (86%) of benzopinacol; m. p. 188–190°. From the experiments with sodium amalgam over 200 g. of benzopinacol has been isolated. Dioxane can be used in place of ethyl ether; the color phenomena and the products are similar to those produced in ordinary ether. When the reaction mixture was hydrolyzed by adding alcohol until no more color remained, no pinacol was obtained; the products were benzophenone and benzohydrol.

Benzopinacol was also obtained by hydrolyzing the mixture resulting from the action of mercury on benzophenone-disodium. The reaction between the mercury and benzophenone-disodium must be

$$2(C_6H_5)_2C\text{—}Na(ONa) + Hg \longrightarrow NaHg + 2(C_6H_5)_2C\text{—}ONa \rightleftarrows (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2$$

The reaction with sodium metal was like that with amalgam. The theoretical amount or a slight excess of sodium in the form of wire was shaken with a solution of benzophenone in ether; glass beads aided in carrying the reaction to completion. At the start of the reaction the sodium wire became red and then quickly changed to blue. After an hour the solution was violet-blue in color and after several days a large amount of precipitate was present. The color obtained with sodium metal was darker than the color formed with sodium amalgam and always had a violet shade even when the ketone was present in excess. The yields of pinacol were usually somewhat smaller than those obtained by using sodium amalgam.

A search of the literature revealed that the formation of benzopinacol had at times been observed by several investigators. Thus, Beckmann and Paul reported that hydrolysis of the sodium derivative of benzophenone gave either a mixture of benzophenone and benzohydrol or else a mixture of these two products in addition to benzopinacol. They made the curious statement that the formation of benzopinacol depends upon the amount of water used for hydrolysis and upon the time taken to isolate the products; only when a large amount of water and a short period of time are employed is it possible to isolate pinacol. We are now in a position to explain this strange statement. If a small amount of water is used, then the great concentration of alkali formed on hydrolysis can decompose the pinacol; this decomposition is favored if the pinacol is allowed to remain in contact with the alkaline solution for a long time. By employing a large amount of water, a weak solution of alkali is obtained and some pinacol remains. The results of Beckmann and Paul[13] and especially of Acree,[14] who reported a 60% yield of benzopinacol, have been neglected in formulating the ketyl theory.

Reaction of Benzophenone with Lithium, Potassium, Rubidium and Cesium.—In like manner, benzopinacol was obtained by hydrolysis of the reaction mixtures obtained from benzophenone and lithium and potassium, free and in the form of amal-

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[12] Cohen [*Rec. trav. chim* , 38, 72 (1919)] found that 10 cc. of 80% alcohol can dissolve 3.5 g. of benzohydrol. We have found that it is also capable of dissolving 3.5 g of benzophenone in addition to the benzohydrol already present.

[13] Schlenk originally considered that small amounts of pinacol might be formed by association of the diphenylhydroxymethyl radicals formed on hydrolysis of the ketyl radicals.

[14] Acree, *Am. Chem. J.*, 29, 588 (1903). See also Tingle and Gorsline, THIS JOURNAL, 30, 1880 (1908), who obtained a 6.5% yield of pinacol.

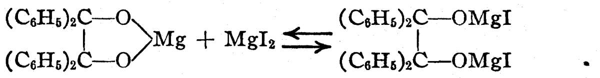
gams. The color of the lithium compound was pale green and at times it seemed to be nearly colorless.

For the reaction with rubidium a liquid amalgam was prepared from 1.0 g. of rubidium and 20 g. of mercury; with benzophenone in ether an intense blue color was produced. Hydrolysis of the solution yielded benzopinacol. Similarly an intense blue color was formed when the liquid amalgam from 0.25 g. of cesium and 25 g. of mercury was shaken with benzophenone in ether; benzopinacol was isolated from the hydrolyzed mixture.

Reaction of Benzophenone with Calcium Amalgam.—Mixtures of 5 to 6 g. of benzophenone and 80 g. of 1% calcium amalgam in 125 cc. of ether were shaken for two weeks. The solution became dark green in color and after several days deposited a large amount of dark green crystals; after two weeks the solid was reddish-brown in color. Hydrolysis gave an 87% yield of benzopinacol.

Reaction of Benzophenone with Magnesium Amalgam.—Magnesium amalgam was prepared from 0.24 g. of magnesium ribbon and 36 g. of mercury heated under toluene; about twenty minutes was required for complete combination. The amalgam of this concentration is semi-liquid. The amalgam was added to a solution of 3.0 g. of benzophenone in 60 cc. of ether. After fifteen minutes of shaking the solution was blue and this color remained for a week; after twelve days the color was red. The yields of pinacol obtained after two days of shaking were 80% of the theoretical amount. Longer shaking seemed to decrease the yield. Perhaps the failure to obtain benzopinacol in our first experiments[6] with magnesium amalgam was due to the solid amalgam which was used; the amalgam probably became coated with magnesium oxide and the reaction was prevented. The low yields (6–7%) of pinacol obtained by Gilman and Brown[15] are explainable on the same basis. By employing the semi-liquid amalgam and shaking the mixture to expose fresh surfaces good yields of pinacol are obtained.

If a colorless solution of magnesium iodide is added to the blue solution obtained from benzophenone and magnesium amalgam, the blue color immediately changes to a cherry-red color which is like that obtained by the action of magnesium and magnesium iodide on benzophenone. The reaction is considered to be



$$\begin{matrix}(C_6H_5)_2C-O\\ | \\ (C_6H_5)_2C-O\end{matrix}\!>\!Mg + MgI_2 \leftrightarrows \begin{matrix}(C_6H_5)_2C-OMgI\\ | \\ (C_6H_5)_2C-OMgI\end{matrix} \qquad (4)$$

followed by a slight dissociation of the iodomagnesium pinacolate into the red iodomagnesium-ketyl radicals, $(C_6H_5)_2C-OMgI$. Furthermore, the same red color and no blue color results when benzophenone is reduced by a mixture of magnesium amalgam and magnesium iodide.

On the basis of color Bergmann and Schuchardt[16] decided that the red color of solutions of iodomagnesium pinacolate cannot be attributed to iodomagnesium-ketyls but to a magnesium compound, $(C_6H_5)_2COMg$, similar to benzophenone-disodium. Contrary to this view is the fact that the red color is formed from the start of the reaction; this means that the red compound is stable in the presence of a large excess of ketone, a circumstance that would be highly improbable if the red compound is like benzophenone-disodium and is similar to a Grignard reagent. Bergrnann's prediction that if the compound, R_2COMgI, were formed it would remain in the monomolecular state like the sodium-ketyls and not associate to the pinacolate no longer has any weight since we have shown that even the sodium compounds are dimolecular.

The entire amount of iodomagnesium pinacolate can be converted by iodine to ketone and not only an amount corresponding to the quantity of colored material present

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[15] Gilman and Brown, THIS JOURNAL 63, 1128 (1930).

[16] Bergmann and Schuchardt, Ann., 487, 285 (1931).

as Bergmann supposed. If the color were due to the presence of a small amount of magnesium compound, and if the color is destroyed by the action of iodine, then the solution should become colorless and remain so. As a matter of fact the red color continues to reappear *throughout* the solution; this occurs even after 90% of the pinacolate has been converted to ketone by the action of iodine, a fact explainable only by assuming that the colored compound is derived continuously from the pinacolate.

Finally, Bergmann's supposition that the formation of the red color when a Grignard reagent is added to a solution of pinacol is due to metallic magnesium that cannot be removed completely from the Grignard reagent is far from correct. By filtration of a Grignard reagent through hardened filter paper a solution can be obtained which is entirely free of suspended particles. This is especially easy to accomplish if one uses, as we do, pure, distilled magnesium[17] either in the form of rods or heavy ribbon. By means of this pure magnesium it is possible to prepare a *colorless* solution of ethylmagnesium iodide. If this colorless solution is filtered onto a solution of benzopinacol, a red colored solution is obtained which contains the equilibrium mixture: $R_2C(OMgI)\text{-}(IMgO)CR_2 \rightleftarrows 2R_2C\text{—}OMgI$

Too much weight must not be placed on mere color phenomena in interpreting the structures of the metallo compounds. It is generally considered that the color of the sodium compounds is the color of the ketyl radicals; in fact the colors have been cited as proof of the radical nature of the compounds. In view of our results, may not the color be attributed to a quinonoid form of sodium pinacolate? The whole question of the origin of the color of the compounds is obscure; how little we know of the cause of the color is exemplified by the fact that the ketone-disodium compounds are likewise intensely colored.

Reaction of Fluorenone with Sodium.—Fluorenone was allowed to react with the calculated amount of sodium wire in the same manner as described for benzophenone. After a short time a heavy dark green precipitate was formed; this appeared to be a complex formed between the ketone and the sodium derivative because the solid disappeared as the reaction proceeded further. After twenty-four hours a large amount of muddy green solid was present; after three days the solution was dark green and contained a green precipitate. From the reaction between 5.0 g. of fluorenone and 0.64 g. of sodium wire there was obtained by hydrolysis after ten days a pale yellow solid which was found to consist of fluorenopinacol and a small amount of fluorenone. The fluorenopinacol was obtained in the form of colorless prisms by recrystallization of the mixture from benzene and alcohol; yield, 4.8 g. (95%); m. p. 188–190°. The compound was identical with the pinacol prepared from fluorenone by reduction by magnesium and magnesium iodide.[6]

In one experiment 6.0 g. of fluorenone was allowed to react with 1.0 g. (30% excess) of sodium. After thirteen days of shaking the mixture was hydrolyzed; it yielded 75% pinacol, 24% fluorenol and 1% of fluorenone; calculated, 70% pinacol and 30% fluorenol. When the crude product was recrystallized from alcohol two kinds of crystals were obtained; one kind was pinacol, the other form melted at 151°. This latter compound was found to be a complex produced by combination of fluorenol and fluorenopinacol and is similar to the complex which is formed between fluorenone and fluorenopinacol.[6] The proportions of each constituent present in the complex were determined by treating 1.08 g. of the compound with a solution of sodium ethylate; under these conditions the pinacol was converted to a mixture of fluorenone and fluorenol. The mixture of ketone and hydrol was separated by recrystallization from benzene, from which the fluorenol crystallizes with benzene of crystallization. The weights of fluore-

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(17) This magnesium, which is 99.7% pure, is made by the Aluminum Company of America, Niagara Falls, N. Y. This pure magnesium is recommended for making Grignard reagents having a high degree of purity.

none (0.38 g.) and of fluorenol (0.72 g.) obtained by this method indicated that the complex consists of one mole of pinacol to one mole of fluorenol. This result was confirmed by recrystallizing mixtures of different proportions of pinacol and fluorenol from benzene. From the mixture of two parts by weight (one mole) of pinacol to one part (one mole) of fluorenol, only the complex of melting point 151° was obtained; other proportions gave mixtures of the complex and one of the components.

Reaction of **2,2′-Dibenzoylbiphenyl** with Sodium.—A mixture of 1.5 g. of 2,2′-dibenzoylbiphenyl and 80 g. of 2% sodium amalgam in 70 cc. of ether was shaken for four days. In this time no trace of color developed; a large amount of the sodium pinacolate was present as a colorless solid. The product which was obtained on hydrolysis of the mixture consisted of 1.1 g. (73%) of 9,10-diphenyldihydrophenanthrenediol of m. p. 202" and 0.4 g. (27%) of the stereoisomer of m. p. 178–179°. The mixture was separated by repeated recrystallization from methyl alcohol in which the lower melting isomer is more soluble than the other. The same products in similar proportions are obtained by reducing dibenzoylbiphenyl by a mixture of magnesium and magnesium iodide.[18] It is clear that the reductions by sodium and by the binary system are of the same nature.

It was found that the pinacol is unaffected by sodium alcoholate, unlike most pinacols. When 0.5 g. of pinacol was shaken with a solution of sodium alcoholate in ether and benzene no decomposition of the pinacol occurred in three hours. The stability of the pinacol is shown by the fact that it can be prepared from dibenzoylbiphenyl by reduction by zinc dust in potassium hydroxide solution.

Reaction of **4-Phenylbenzophenone** and **4,4′-Diphenylbenzophenone** with Sodium.—Five to ten gram portions of 4-phenylbenzophenone and 100 g. of 2% sodium amalgam in 120 cc. of ether were shaken for three weeks. In a short time an intensely colored blue-green solid appeared (complex). After some time this solid disappeared and a bright emerald-green mixture resulted which contained a light green precipitate. When the mixture was run into dilute acetic acid a large amount of pinacol precipitated. This was filtered off, washed with acetone and recrystallized from a mixture of chloroform and acetone, from which it was obtained in the form of colorless needles; m. p. 198°. In one experiment in which 6.0 g. of ketone had reacted, 5.5 g. (90%) of the pinacol was obtained. The product was found to be identical with 4,4′-diphenylbenzopinacol that is formed by reduction of the ketone by magnesium and magnesium iodide.[6] The result is of especial interest since the potassium derivative of this ketone was used by Schlenk in molecular weight determinations and was interpreted as being monomolecular.

In a similar manner 4,4′,4″,4‴-tetraphenylbenzopinacol was obtained in 70% yields by hydrolysis of the sodium derivative of diphenylbenzophenone. When the solid pinacol was treated with a solution of sodium ethylate a green color was produced and the pinacol was cleaved into a mixture of ketone and hydrol.

Although Schlenk and Weickel stated that benzene solutions of the sodium derivatives of the ketones are unfortunately colloidal so that the structures could not be determined by molecular weight determinations but only from the reactions of the compounds, nevertheless, Schlenk and Thal made use of determinations of the molecular weight in ether to prove that the compounds are monomolecular. In addition to the probability that the ether solutions are likewise colloidal there arises the question whether the reaction between the ketone and the metal was complete. This is important when one considers that a difference of less than one-tenth of a degree elevation in the boiling point determined whether the compound was completely monomolecular or entirely dimolecular. We have carried out an experiment which shows that the results of the determinations are of doubtful value. We have shaken in a sealed tube in an atmos-

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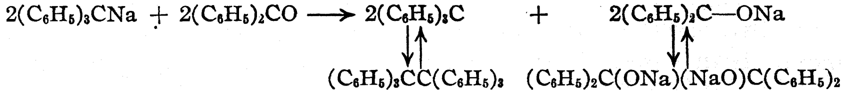
(18) Bachmann, THIS JOURNAL, 54, 1969 (1932).

phere of nitrogen a mixture of 0.2144 g. of 4-phenylbenzophenone and 0.035 g. of potassium in 17.5 g. of ether, the exact proportions used by Schlenk in a molecular weight determination. After the mixture had been shaken for a few days a considerable amount of potassium pinacolate was present as an insoluble precipitate. This precipitate did not dissolve when the mixture was warmed to the boiling point of the solution. These results show that Schlenk and Thal either had not carried out the reaction to completion or else had supersaturated solutions. In either case the determinations would have no value.

Conclusion

All of the reactions of the sodium derivatives of the ketones that have been studied so far are in harmony with our view that the compounds are chiefly sodium pinacolates. We are now examining the reactions of the compounds with a variety of reagents and we shall publish the results in the near future. It is not unlikely that the structures of the compounds formed by the action of sodium on ketones in liquid ammonia[19] are likewise dimolecular; at any rate a reexamination of the products from this point of view may prove of value.

The reaction between sodium triphenylmethyl and benzophenone must now be considered to be analogous to the reaction between triphenylmethylmagnesium bromide and benzophenone[20] which yields triphenylmethyl and bromomagnesium pinacolate; the sodium triphenylmethyl reaction should now be written



$$\begin{array}{ccccc} 2(C_6H_5)_3CNa + 2(C_6H_5)_2CO & \longrightarrow & 2(C_6H_5)_3C & + & 2(C_6H_5)_2C{-}ONa \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & (C_6H_5)_3CC(C_6H_5)_3 & & (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2 \end{array}$$

In our opinion many or all of the compounds obtained by addition of potassium to benzopinacolone, phenanthrenequinone, dimethylpyrone, etc., are not ketyls as Schlenk supposes but are sodium pinacolates or related compounds. We are examining these compounds from this viewpoint.

Finally we are studying the action of metals, free and in the form of amalgams, on aldehydes, esters and other compounds in the hope of clearing up the reactions undergone by these compounds.

Summary

The products obtained by the action of sodium on aromatic ketones in anhydrous ether are chiefly sodium pinacolates, $R_2C(ONa)(NaO)CR_2$, and not free ketyl radicals, $R_2C{-}ONa$, existing in the monomolecular state as has been supposed up to this time.

Hydrolysis of the sodium pinacolates with dilute acid gives pinacols in excellent yields. In order to account for the reactions of the pinacolates with certain reagents it is assumed that the pinacolate is in equilibrium

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[19] Wooster, THIS JOURNAL, 50, 1388 (1928), concluded that in liquid ammonia the monosodium derivative appears to be a typical radical in accordance with the views of Schlenk.

[20] Bachmann, *ibid.*, 53, 2758 (1931).

with small amounts of ketyl radicals, $2R_2C—ONa \rightleftarrows R_2C(ONa)(NaO)$-$CR_2$. The ketyl radicals are intermediates in the reduction of the ketone to the pinacolate.

Other metals such as lithium, potassium, rubidium, cesium, beryllium, magnesium and calcium react in the manner of sodium. In all cases the products are metal pinacolates which differ from the sodium pinacolate and from each other only in degree.

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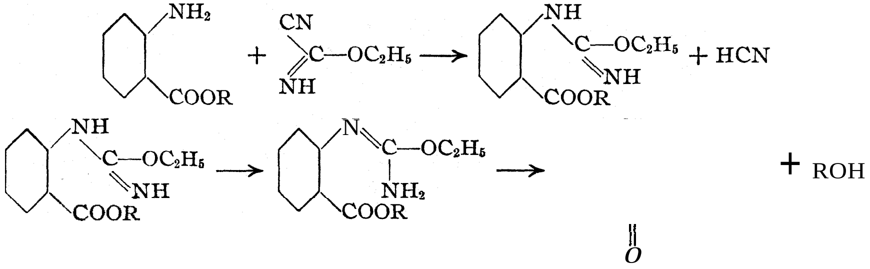
Quinazolines. V. The Partial Hydrolysis of 2,4-Dialkoxyquinazolines with the Formation of 2-Alkoxy-4-ketodihydroquinazolines

BY N. A. LANGE AND F. E. SHEIBLEY

The earliest derivatives of quinazoline on record were prepared by Peter Griess in 1869. By the action of cyanogen on anthranilic acid in alcoholic solution he obtained 2-ethoxy4-ketodihydroquinazoline, and from this, through hydrolysis with hydrochloric acid, benzoylene urea.[1] In 1910 Finger and Zeh[2] condensed cyanimidocarbonic acid ethyl ester with methyl and ethyl anthranilates, and found that the products were the same in both cases. Their compound was subsequently shown to be identical with the 2-ethoxy-4-ketodihydroquinazoline of Griess, and the reactions leading to its formation were explained as follows[3]



Griess' reaction probably follows a similar course, the addition product, $(CN)_2NH_2C_6H_4COOH$, first formed losing HCN to form a N-cyanoanthranilic acid, which then adds alcohol and rearranges as indicated, the 3,4-dihydro structure[4] being preferred since the substance, on methylation followed by hydrolysis, is transformed into 3-methylbenzoylene urea.[5]

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(1) Griess, Ber., 2, 415 (1869).

(2) Finger and Zeh, *J. prakt. Chem.*, [2] 81, 468 (1910).

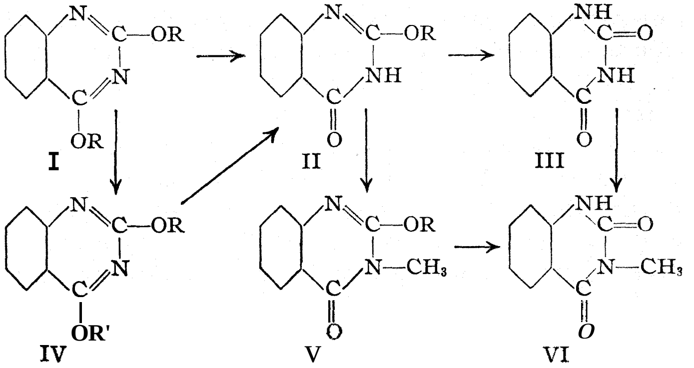
(3) Finger and Günzler, Berichtigung, *ibid.*, [2] 83, 198 (1911).

(4) See also Bogert and Gortner, THIS JOURNAL, 32, 123 (1910).

(5) Finger, J. prakt. *Chem*, [2] 81, 470 (1910).

With a view of confirming the alcohol splitting and subsequent ring closure at the anthranilic ester portion of the molecule, as written above, rather than the explanation originally proposed by Finger and Zeh,[6] McKee[7] in 1911, treated ethyl anthranilate with cyanimidocarbonic acid methyl ester and obtained the expected 2-methoxy-4-ketodihydroquinazoline. This compound possessed properties similar to those of the ethoxy derivative of Griess and of Finger and Zeh, and like the ethoxy derivative was readily hydrolyzed to benzoylene urea.

The synthesis to be described may be considered as a reversal of the original synthesis of Griess, as well as that of Finger and Zeh, since by the alkaline hydrolysis of 2,4-diethoxyquinazoline, prepared from benzoylene urea through the intermediate 2,4-dichloroquinazoline, 2-ethoxy-4-ketodihydroquinazoline is obtained. The ester-like character of the 4-alkoxy group as compared with a similar ether substituent in the 2-position of quinazoline is also demonstrated. When 2,4-diethoxyquinazoline (I) is warmed with a methyl alcoholic solution of sodium methylate, a mixed quinazoline diether, 2-ethoxy-4-methoxyquinazoline(IV) results.[8]



Where R = C_2H_5 then R′ = CH_3, or when R = CH_3 then R' = C_2H_5

On prolonging this treatment, however, the yield of the mixed diether gradually decreases and an alkali-soluble product, 2-ethoxy-4-ketodihydroquinazoline (II), is formed. By substituting alcoholic sodium ethylate for the sodium methylate the same product is obtained directly from diethoxyquinazoline (I), without any intermediate mixed diether formation taking place.[9] The 2-ethoxy-4-ketodihydroquinazoline(II) thus prepared, possesses all of the properties previously recorded for this substance and, in the presence of hydrochloric acid, is easily hydrolyzed to benzoylene urea (III). It reacts readily with dimethyl sulfate to give 2-ethoxy-3-methyl-4-ketodihydroquinazoline (V), the properties of which agree with those previously

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(6) Ref. 2, p. 466.

(7) McKee, *ibid.*, [2] 84, 821 (1911).

(8) Lange and Sheibley, THIS JOURNAL, 54, 4306 (1932).

(9) The hydrolyzing action is due, of course, to the small amount of water present. When the better grades of absolute alcohols were used only a very slight hydrolysis occurred.

described by Finger[5] for the same substance. Hydrolysis with hydrochloric acid now gives 3-methylbenzoylene urea (VI), identical with the same compound prepared directly from benzoylene urea (III) by methylation with methyl iodide and alkali.[10]

2-Ethoxy-4-ketodihydroquinazoline(II) being a known substance, therefore, the position of the partial hydrolysis of diethoxyquinazoline (I) under alkaline conditions is indicated, and the constitution of 2-ethoxy-4-methoxyquinazoline (IV) follows. The isomeric mixed diether, 2-methoxy-4-ethoxyquinazoline,[8] must, by elimination, be as represented, since it is the second of two possibilities in a discussion limited to 2,4-diethers only. This view is confirmed by an analogous system of reactions, starting with 2,4-dimethoxyquinazoline. When this substance (T) is subjected to prolonged boiling with alcoholic sodium ethylate or methyl alcoholic sodium methylate it is converted into 2-methoxy-4-ketodihydroquinazoline (11), 2-methoxy-4-ethoxyquinazoline (IV) being an intermediate product when the former reagent is employed. The 2-methoxy-4-ketodihydroquinazoline (II) thus obtained had a constant melting point of 218° for different preparations and was hydrolyzed smoothly to benzoylene urea (III) by dilute hydrochloric acid. The methoxy keto compound described by McKee, on the other hand, melted at 231–232°; his experiment was, therefore, repeated when a product melting at 226° after crystallization from alcohol was obtained. The accidental isolation, in an earlier experiment, of an apparently higher melting 2-ethoxy-4-ketodihydroquinazoline suggested that the hydrolysis product and the substance obtained by repeating McKee's experiment were nevertheless the same, and the problem resolved itself into showing that the two compounds with different melting points were yet identical. This was accomplished through methylation, both products (II) being converted into a new substance, 2-methoxy-3-methyl-4-ketodihydroquinazole (V), on treatment with dimethyl sulfate. The new compound (V) was then subjected to acid hydrolysis and 3-methylbenzoylene urea (VI) obtained in both cases. That the variation in melting points is due to small amounts of benzoylene urea being present and affecting the temperature of the decomposition into benzoylene urea which ensues upon melting, remains a matter of conjecture. By condensing cyanimidocarbonic acid methyl ester with methyl anthranilate instead of the ethyl anthranilate employed by McKee, 2-methoxy-4-ketodihydroquinazolineidentical, even to the melting point, with the same substance produced by the alkaline hydrolysis method, was obtained.

Two other isolated instances of the same partial hydrolysis in the presence of alkali were also observed. Attempts to remove the chlorine of 2-chloro-4-ethoxyquinazoline by treatment with dilute acids resulted only

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(10) Bogert and Scatchard, THIS JOURNAL, 41, 2062 (19191.

in the formation of benzoylene urea, and showed that the compound is totally unstable under these conditions. When it is boiled with alcoholic potash, however, only the ethoxy group is removed, and 2-chloro-4-ketodihydroquinazoline is formed. Similarly, 2,4-diphenoxyquinazoline, on warming with alcoholic potash, is transformed into 2-phenoxy-4-ethoxyquinazoline,[8] a slow hydrolysis to 2-phenoxy-4-ketodihydroquinazoline then taking place. By substituting sodium ethylate in alcohol for the alcoholic potash a more rapid hydrolysis is realized, both the phenoxyethoxy derivative and its methoxy analog being converted into 2-phenoxy-4-ketodihydroquinazoline.

All melting points given in this paper are corrected.

Experimental Part

The 2,4-dialkoxyquinazolines (I) used in these experiments were prepared by dissolving just two molecular proportions of sodium in a convenient volume of the absolute alcohol, adding a slight excess over one molecular proportion of 2,4-dichloroquinazoline, and refluxing on a steam-bath for two hours. The cooled solution was poured into a large excess of water and the precipitated dialkoxyquinazoline filtered off and crystallized from alcohol. In the following experiments 95% alcohols were employed unless otherwise stated.

Preparation of **2-Ethoxy-4-ketodihydroquinazoline (II).**—Four grams of 2,4-diethoxyquinazoline in 20 cc. of alcohol was added to 0.5 g. of sodium dissolved in 20 cc. of alcohol and the mixture gently boiled on a steam-bath for six hours. On cooling, it was poured into 200 cc. of water and the clear solution made just acid with acetic acid. The 3.3 g. of precipitate that separated was crystallized from alcohol, forming long colorless glistening needles, m. p. 179°. When methyl alcohol was used in place of the ethyl alcohol, the same product was obtained. With shorter periods of heating or when absolute alcohols were employed the hydrolysis was incomplete, and on pouring into water some unchanged diethoxyquinazoline, or 2-ethoxy-4methoxyquinazoline when methyl alcohol was used, precipitated.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.12: H, 5.30. Found: C, 63.46: H, 5.25.

The substance, on warming with a little hydrochloric acid in alcohol, was completely hydrolyzed to benzoylene urea, m. p. 351°. On methylation with dimethyl sulfate the product described by Finger, 2-ethoxy-3-methyl4ketodihydroquinazoline (V), was obtained. Seven-tenths gram of 2-ethoxy-4-ketodihydroquinazoline dissolved in 10 cc. of normal sodium hydroxide was treated with 1 cc. of dimethyl sulfate and allowed to stand for twenty-four hours. The 0.6 g. of precipitate that separated crystallized from dilute alcohol in small prisms, m. p. 75–76°, and on warming with dilute hydrochloric acid was readily hydrolyzed to 3-methylbenzoyleneurea, m. p. 242°.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: C, 64.67; H, 5.93. Found: C, 65.20; H, 6.05.

In one preliminary experiment in which diethoxyquinazoline was boiled with absolute methyl alcoholic sodium methylate for eight hours, a substance crystallizing from alcohol in small needles, m. p. 202–205°, was obtained. This material is apparently a higher melting variety of 2-ethoxy-4-ketodihydroquinazoline, but attempts to produce it again were unsuccessful, the normal form of the compound (m. p. 179°) always resulting. When it was mixed with the latter the melting point was 185°, and hydrolysis with dilute hydrochloric acid gave benzoylene urea as before. On methylation with dimethyl sulfate a partial hydrolysis occurred and a pasty product (m. p. 190–220° and 217–230° after an attempted purification), which, however, gave pure 3-methylbenzoylene urea on hydrolysis, was formed. Specimens of the normal compound melting at 179°, when contaminated with a small amount of benzoylene urea, underwent a slight lowering of the melting point.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.12; H, 5.30. Found: C, 62.74; H, 4.98; C, 62.65; H, 5.24.

Preparation of 2-Methoxy-4-ketodihydroquinazoline (II).—Four grams of 2,4-dimethoxyquinazoline and 0.5 g. of sodium, each dissolved in 20 cc. of methyl alcohol, were mixed and the solution boiled gently on a steam-bath for five hours. At the end of this time the cold solution was poured into 200 cc. of water and the 1.2 g. of unchanged dimethoxyquinazoline that precipitated was removed by filtration. The filtrate, acidified with acetic acid, yielded 2.1 g. of crude 2-methoxy-4-ketodihydroquinazoline, a further quantity of more impure material being obtained by salting out the final acid filtrate. Crystallization from alcohol gave short colorless needles, m. p. 218°. On warming an alcoholic solution of the substance with a little hydrochloric acid, benzoylene urea, m. p. 352°, precipitated. When 1.2 g. of dimethoxyquinazoline and 0.2 g. of sodium in 40 cc. of alcohol was boiled for five hours the hydrolysis was complete, the yield of precipitated 2-methoxy-4-ketodihydroquinazoline amounting to 1.0 g. As in the case of the ethoxy derivative, only a slight hydrolysis occurred when absolute alcohols were used as solvents.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.34; H, 4.58. Found: C, 61.90; H, 4.61; C, 61.71; H, 4.78.

Preparation of 2-Methoxy-3-methyl-4-ketodihydroquinazole (V).—To 1.15 g. of **2-methoxy-4-ketodihydroquinazoline** dissolved in 20 cc. of normal sodium hydroxide solution was added 2 cc. of dimethyl sulfate, and the mixture allowed to stand with occasional shaking, an alkaline reaction being maintained by adding small amounts of sodium hydroxide solution whenever necessary. A precipitate began to form immediately and within a few hours had filled the whole solution. After six hours the mixture was warmed on a water-bath to decompose any traces of dimethyl sulfate, the precipitate melting to a more compact mass. This was resolidified by cooling in running water for a few minutes, removed by filtration and dried, and weighed 1.0 g. Crystallization from dilute alcohol yielded 0.85 g. of small white needles, m. p. 93°, with a faint but pleasant odor similar to that of 2,4-dimethoxyquinazoline. The substance dissolved readily in warm dilute hydrochloric acid from which solution, after a few minutes, fine needles of 3-methylbenzoylene urea, m. p. 242°, separated. This hydrolysis product is evidently quite pure, for specimens of 3-methylbenzoylene urea obtained from the hydrolyses of 2-ethoxy-3-methyl-4-ketodihydroquinazoline described above also had m. p. 242°, the melting point of 3-methylbenzoylene urea recorded by previous investigators[10] being 237–238°. A mixed melting point using a sample of 3-methylbenzoylene urea prepared from benzoylene urea and methyl iodide following their procedure, confirmed the identity of the hydrolyzed products.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.12; H, 5.30. Found: C, 63.50; H, 5.44.

Preparation of **2-Methoxy-4-ketodihydroquinazoline** by **the** Direct **Method.**[7]—Cyanimidocarbonic acid methyl ester, $HN{=}C(CN)OCH_3$, was prepared by McKee's modification of the method employed by Nef[11] in preparing the corresponding ethyl ester. The product was a colorless refractive oil with an odor similar to that of 2.4-dichloroquinazoline or of acetamide, and boiled around 50° at 40 mm. pressure. Six grams of the ester was mixed with 17 g. of ethyl anthranilate and 2.5 g. of cuprous chloride and the mixture immersed in water at 80°, since on gradually heating it to this temperature the reaction followed a different course and unknown products were formed. The 2-methoxy-4-ketodihydroquinazoline was isolated by following McKee's

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(11) Nef, *Ann.*, 287, 296 (1895).

procedure. Short colorless needles, m. p. 225°, and identical in appearance with the 2-methoxy-4-ketodihydroquinazoline prepared by the alkaline hydrolysis of dimethoxyquinazoline, were obtained.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.34; H, 4.58. Found: C, 61.10; H, 4.74.

The substance was further purified by dissolving it in sodium hydroxide solution, reprecipitating with acetic acid, and recrystallizing from alcohol. m. p. 226''. When it was mixed with a specimen of the above-mentioned hydrolysis product, m. p. 218°, the melting point was 224°. These melting points are not strictly constant, however, and appear to be decomposition temperatures as well as melting points. The compound does not melt to a clear liquid but rather to a mush which only clears at much higher temperatures, and on cooling and reheating melts far above *the original melting* point. McKee gives the melting point as 231–232° followed by decomposition into benzoylene urea. The 2-methoxy-4-ketodihydroquinazoline prepared by hydrolysis behaved similarly except that the melting point of different preparations was constant (218'). The higher melting variety (226'') by the direct method was, therefore, treated with dimethyl sulfate and a product identical (mixed melting point) with the 2-methoxy-3-methyl-4-ketodihydroquinazoline already prepared by the corresponding methylation of the hydrolysis product, was obtained. This sample, on hydrolysis with dilute hydrochloric acid, also gave 3-methylbenzoylene urea as before, the latter being again identified by mixed melting points with known specimens of 3-methylbenzoylene urea.

A final confirmation of the identity of 2-methoxy-4-ketodihydroquinazoline when prepared by either the direct or the hydrolysis method was afforded by substituting methyl anthranilate for the ethyl anthranilate and repeating the condensation with cyanimidocarbonic acid methyl ester as described above. The product in this case formed colorless needles, m. p. 218°, and was identical in appearance with the alkaline hydrolysis product, m. p. 218°. When it was mixed with the latter there was no depression of the melting point.

Preparation of 2-Chloro-4-ketodihydroquinazoline, $\overline{NH{-}CO{-}C_6H_4N{=}C}Cl$, from 2-Chloro-4-ethoxyquinazoline.—One gram of 2-chloro-4-ethoxyquinazoline was dissolved in a lukewarm solution of 0.3 g. of potassium hydroxide in 25 cc. of alcohol and the solution allowed to stand overnight. It was then warmed for an hour and finally diluted with 100 cc. of water which precipitated 0.15 g. of unchanged chloroethoxyquinazoline. The filtrate from this precipitate had a turbid appearance and a neutral reaction; on acidifying it with acetic acid 0.6 g. of 2-chloro-4-ketodihydroquinazoline separated and was collected and dried. The substance is sparingly soluble in alcohol and crystallizes in feathery needles, m. p. 212''; when it was warmed with alcoholic aniline, 2-anilino-4-ketodihydroquinazoline[12] was formed. A second specimen of chloroketodihydroquinazoline, prepared by rubbing 2,4-dichloroquinazoline with normal sodium hydroxide solution,[13] diluting with water, filtering and acidifying the filtrate with acetic acid as before, also had m. p. 212°, and did not depress the melting point of the first product. Small amounts of the chloroketo compound were likewise obtained as a by-product in the preparation of diethoxyquinazoline from dichloroquinazoline by acidifying the aqueous filtrates remaining after the water precipitation already described for isolating the dialkoxy compound. For a general method of preparation, however, the procedure employing dichloroquinazoline and sodium hydroxide in aqueous solution is both simple and direct and gives the best yields of an easily purified product. The chloroketodihydroquinazoline obtained by boiling dichloroquinazoline in alcoholic solution with sodium acetate is at best a by-product, and is difficult to purify.[14]

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(12) Lange and Sheibley, THIS JOURNAL, 64, 1997 (1932).

(13) British Patent 287,179.

(14) Lange and Sheibley, THIS JOURNAL, 53, 3871 (1931).

For analysis the substance was simply warmed with dilute nitric acid for a few minutes or until the decomposition appeared to be complete, and the benzoylene urea removed by filtration and weighed, chlorine being determined gravimetrically on the filtrate; recovered: 93.6% of the theoretical amount of benzoylene urea.

Anal. Calcd. for $C_8H_5ON_2Cl$: Cl, 19.64. Found: Cl, 19.45.

Preparation **of 2-Phenoxy-4-ketodihydroquinazoline,** $\overline{\mathrm{NH{-}CO{-}C_6H_4N{=}C}}\mathrm{OC_6H_5}$.—One gram of 2,4-diphenoxyquinazoline was added to 0.2 g. of potassium hydroxide dissolved in 25 cc. of alcohol and the mixture warmed on the steam-bath for four hours, the diphenoxy compound dissolving completely in about half this time. The solution was allowed to cool and diluted with 100 cc. of water, the white opaque suspension which resulted coagulating within a day or so to 0.7 g. of 2-phenoxy-4-ethoxyquinazoline. The filtrate, after removal of the ethoxy derivative, was acidified with acetic acid and 0.1 g. of 2-phenoxy-4-ketodihydroquinazoline thus precipitated.

The 0.7 g. of phenoxyethoxyquinazoline in 25 cc. of alcohol containing 0.2 g. of sodium was warmed for four and one-half hours, allowed to cool, and diluted with 80 cc. of water. After adding **3** cc. of normal sodium hydroxide, the solution was boiled to remove most of the alcohol and filtered hot from a trace of precipitate. Acidification of the cold solution as above precipitated 0.65 g. of the product. The 0 75 g of 2-phenoxy-4-ketodihydroquinazoline thus obtained was crystallized from about 70 cc. of hot alcohol, in which it is somewhat more soluble than the corresponding 2-anilino-4-ketodihydroquinazoline, and separated in glistening silky hair-like needles, m. p. 272°; yield 0.65 *g*. The compound is soluble with decomposition in warm dilute (1:1) hydrochloric acid, from which solution needles of benzoylene urea separate on cooling.

Anal. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.56; H, 4 23. Found: C, 70 99; H, 4.58.

Summary

Alkaline conditions have been found to effect a partial hydrolysis of 2,4-dialkoxyquinazolines with the formation of 2-alkoxy-4-ketodihydroquinazolines. These products are shown to be identical with the same substances produced previously by methods involving a ring closure, and demonstrate conclusively the constitutions of 2-ethoxy-4-methoxyquinazoline and 2-methoxy-4-ethoxyquinazoline. Similarly, 2-chloro-4-ethoxyquinazoline and 2-phenoxy-4-alkoxyquinazolines are hydrolyzed to 2-chloro-4-ketodihydroquinazoline and 2-phenoxy-4-ketodihydroquinazoline, respectively. Two new compounds, 2-methoxy-3-methyl-4-ketodihydroquinazoline and 2-phenoxy-4-ketodihydroquinazoline, have been prepared.

CLEVELAND, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

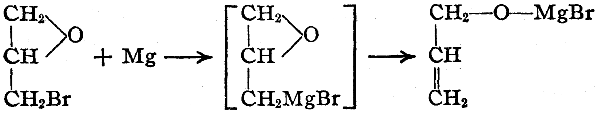
Furan Reactions. VI. Cyclopropene

BY CHARLES D. HURD AND FORREST D. PILGRIM

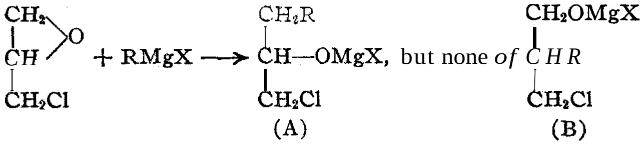
Cyclopropene has been prepared by Demjanov and Dojarenko[1] by pyrolyzing cyclopropyltrimethylammonium hydroxide. Its dibromide was stated to boil at 45° (27 mm.) and its tetrabromide at 155° (19 mm.). Cyclopropene was earlier mentioned by Freundler,[2] who reported having obtained it (as the bromide derivative) in the pyrolysis of barium furoate or calcium furoate. Freundler did not isolate cyclopropene as such. Cyclopropene was sought for in the products of electrolysis of sodium 1,2-cyclopropanedicarboxylate, but no evidence for it was observed.[3]

Freundler's method seemed attractive to study because of the availability of furoic acid. Accordingly, barium, calcium and sodium furoates were prepared and heated with or without soda lime under varying conditions (Freundler used soda lime). Furan and other products were formed but no appreciable yields of cyclopropene could be realized.

Two other reactions are of interest in this connection. The interaction of epibromohydrin with magnesium gave allyl alcohol



Cyclopropyl alcohol may have been in the reaction products but no definite evidence for it was obtainable. The reason for considering it as a possible reaction product is the analogy it bears to Koelsch and McElvain's[4] observation that Grignard reagents react with epichlorohydrin as follows



In the present work, cyclopropyl alcohol is analogous to (A) and allyl alcohol is analogous to (B), if the —CH_2MgBr group reacts with the ethylene oxide ring of the same molecule.

β,β'-Dibromoisopropyl benzoate, $C_6H_5COOCH(CH_2Br)_2$, was synthesized from dibromohydrin and benzoyl chloride. This compound offers possibilities of change into cyclopropyl benzoate by reaction with zinc, but this was not investigated.

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(1) Demjanov and Dojarenko, *Ber.*, 55, 2718 (1922); 56, 2200 (1923).

(2) Freundler, *Compt. rend.*, 124, 1167 (1897); *Bull. soc. chim.*, [3] 17, 613 (1897).

(3) Fichter and Spiegelberg, *Helv. Chim. Acta*, 12, 1152 (1929).

(4) Koelsch and McElvain, THIS JOURNAL, 51, 3390 (1929); 52, 1164 (1930).

Experimental Part

Barium **Furoate.—Fifty** grams of barium furoate was mixed with 15 g. of soda lime and put in an ordinary distilling flask which was connected in series to a water-cooled condenser, a receiver and a 2 5-liter gas-collecting bottle. The flask was heated by a moving flame, using a wire gauze, until gas evolution ceased. Then another identically charged distilling flask was substituted for the first one and the process repeated till 900 g. of barium furoate (equivalent to 860 g of the anhydrous salt) had been dry-distilled In all, 85 liters of gas was collected. In addition to an aqueous layer which was separated and discarded, about 130 g. of liquid was also collected.

Gas.—The gas was circulated through a coil condenser at −78° whereupon 35–40 cc. of liquid condensate was obtained. There was much uncondensed carbon monoxide. The condensate was fractionated, using a low-pitched, vacuum-jacketed spiral column.[5] Only 2 cc of distillate appeared in the −30° range. The rest was almost entirely furan, 34 g. of which was collected. The 2 cc. of low boiling liquid was vaporized and analyzed by the absorption method.[6] Three-fifths of it dissolved in the acetylene reagent (alkaline K_2HgI_4), showing it to be methylacetylene. This was confirmed by isolating dipropinylmercury,[7] m. p. 202°, as a reaction product. The remaining two-fifths dissolved in 82% sulfuric acid (but not in 62%). Inasmuch as 82% sulfuric acid absorbs quantitatively all olefins which give rise to *sec*-alkyl hydrogen sulfates (such as propylene, *a*- or *β*-butylene, allene, butadiene, etc.) it may be assumed safely that cyclopropene would be absorbed also by this reagent However, even if the absorbed portion were pure cyclopropene, which is extremely doubtful, its yield (which would be about 0.2%) is entirely unsatisfactory.

Liquid.—From the 130 g. of liquid, 90 g. of furan (b. p. 31–33') was obtained, which made a total furan yield of 124 g. In addition, higher boiling liquids were present: (b. p., cc.) 40–50, 6; 50–100, 4; 100 (750)–95 (25 mm.), 7; 95–200 (25 mm.), 10 cc., which turned black as it entered the receiver. The last fraction may have contained difuryl ketone, as Freundler intimated. We did not press this point in view of Reichstein's recent work. Reichstein[8] was unable to isolate any pure difuryl ketone by this method but he did synthesize it in other ways (b. p. 150° at 12 mm.).

Non-production of **Cyclopropene.—No** better yields of cyclopropene were obtained when the heating was performed by a salt-bath at 345°, at which temperature a rapid gas evolution occurred. Also, nothing of interest in this connection was obtained when barium furoate was heated alone without the soda lime. This pyrolysis required careful watching to avoid too vigorous a reaction.

Since Freundler identified the cyclopropene as bromide derivatives, this was next carried out. Accordingly, the gas from 36 g. of barium furoate and 14 g. of soda lime when heated as before was collected over water and then passed[9] through a solution of bromine in chloroform at −10°. On fractionation, 0.5 cc. of a dibromide fraction (b p. 32–40° at 17 mm.; n^{20}_{D} 15360) and 1 cc. of a tetrabromide fraction (b. p. 140–155° at 11 mm ; n^{21}_{D} 1.6192) were isolated. There is no certainty that these derivatives represent cyclopropene but the yield is very small in any event.

Other **Salts.—A** mixture of calcium furoate (36 g.) and soda lime behaved similarly, yielding about 5 liters of gas. This, in turn, gave rise to about 1 cc each of dihromide and tetrabromide derivatives.

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(5) Davis, Ind. *Eng. Chem., Anal. Ed., 1,* 61 (1929).

(6) Hurd and Spence, THIS JOURNAL. 51, 3356 (1929).

(7) Johnson and McEwen, *ibid.*, 48, 469 (1926).

(8) Reichstein, *Helv. Chim. Acta, 13, 356 (1930).*

(9) Trouble was usually encountered when the gas was passed directly into the bromine solution without previously collecting it.

Sodium furoate and soda lime gave more furan and less gas. The cyclopropene content of the gas, as determined by bromination, was small as in the previous cases.

Epibromohydrin.—This reagent was prepared from dibromohydrin using a method similar to that of "Organic Syntheses," Vol. III, for epichlorohydrin.

Two grams of epibromohydrin, 5 cc. of dry ether and 15 g. of turnings of magnesium–copper alloy (12.7% Cu) were placed in a flask. Action was started by a crystal of iodine. The spontaneous refluxing continued as a mixture of 78 g. more of epibromohydrin in 150 cc. of dry ether was added drop by drop. When all was added, it was refluxed for three hours on a water-bath. Then it was hydrolyzed and the ether layer distilled: b. p. 92–100°, 8 cc.; b. p. 60–65° (20 mm.), 6-8 cc.; b. p. 95–96° (15 mm.), 6–8 cc. None of these fractions showed any tendency to crystallize when left at −30° for forty minutes.

Allyl alcohol was confirmed in the 92–100° fraction by mixing 0.6 g. of it with 6 cc. of absolute pyridine and 2.8 g. of triphenylchloromethane. Thus there was formed allyl triphenylmethyl ether,[10] m. p. 74°. A mixed melting point with similar material made from known allyl alcohol was not depressed.

β,β'-Dibromoisopropyl Benzoate.—Forty-four grams of α,α'-dibromohydrin, $(BrCH_2)_2CHOH$, was mixed with 35 g. of benzoyl chloride and warmed until the evolution of hydrogen chloride ceased, usually less than half an hour. Then it was cooled, washed with sodium hydroxide, extracted with ether and distilled twice *in vacuo*. Forty grams of β,β'-dibromoisopropyl benzoate was collected at 185° and 16 mm. This is a 66% yield

This ester did not solidify at −30° in three hours. Its density at 23.5° was 1.6324. The index of refraction values, n_D, were 1.5749 at 4.7° and 1.5658 at 24.8°.

Anal. Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.8. Found: Br, 50.6.

Summary

Attempts to prepare cyclopropene by Freundler's method, namely, the dry distillation of a mixture of barium furoate or calcium furoate with soda lime gave negligible yields. Methylacetylene was identified as a reaction product but also in small amounts. Considerable furan was formed.

Allyl alcohol was produced as a result of the action of magnesium on epibromohydrin. β,β'-Dibromoisopropyl benzoate was synthesized.

EVANSTON, ILLINOIS

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(10) Helferich, Speidel and Toeldte, Ber., 56, 766 (1923).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Distibyls. II. Tetra-*p*-bromotetraphenyl- and Tetra-*p*-tolyldistibyl. Di-α-naphthyliodostibine[1]

BY F. F. BLICKE AND U. O. OAKDALE[2]

It has been shown that tetraphenyldistibyl[3] behaves similarly to tetraaryldiarsyls in that it reacts almost instantly with an amount of oxygen equivalent to that required for the formation of a peroxide. An analogous behavior characterizes the new distibyls which we have prepared—tetra-p-bromotetraphenyl-and tetra-p-tolyldistibyl.

No evidence could be obtained by molecular weight determinations in favor of the assumption that tetraphenyl- or tetra-p-tolyldistibyl dissociates into diarylstibyl radicals.[4]

In the case of di-α-naphthyliodostibine only a few grams of the pure iodide were isolated by a laborious process from five kilograms of α-naphthylamine, hence the corresponding distibyl was not prepared.

The diaryliodostibines, which yielded the distibyls when treated with sodium hypophosphite, were synthesized by means of the following series of reactions: the required aryl amine was diazotized and allowed to react with antimony trichloride, the arylstibinic acid produced was reduced to the aryldichlorostibine and the latter hydrolyzed to the corresponding oxide. The oxide, when heated, was converted into the tetraarylstibyl oxide and antimony trioxide.[5] Treatment with acetic acid converted the tetraarylstibyl oxide into the diarylstibyl acetate; this compound yielded the diaryliodostibine when mixed with hydriodic acid.

Experimental Part

p-Bromophenyldichlorostibine.—*p*-Bromophenylstibinic acid[6] was obtained from p-bromoaniline according to the method used by Dunning and Reid[7] for the preparation of other arylstibinic acids. Two hundred grams of the air-dried acid was dissolved in 500 cc. of cold, concd. hydrochloric acid, the solution stirred and 550 cc. of water added. The flocculent material was removed by filtration and 25 g. of charcoal was added to the red filtrate, the mixture shaken frequently and filtered after twelve hours. The filtrate was cooled with ice and saturated with sulfur dioxide. The *p*-bromophenyldichlorostibine (40–60 g.) which precipitated was air dried and recrystallized from heptane; m. p. 90–92°. The dichloro compound is very soluble in benzene, less soluble in acetic acid.

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(1) This paper represents the third part of a dissertation to be submitted to the Graduate School by Mr. Oakdale in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Parke, Davis and Company Fellow.

(3) Blicke and Oakdale, THIS JOURNAL, 53, 1026 (1931).

(4) Failure to obtain data indicative of dissociation by molecular weight determinations does not prove that distibyls do not dissociate in solution; the degree of dissociation may be of such a low magnitude that it cannot be detected by the ordinary molecular weight procedures.

(6) This series of reactions was developed for the preparation of organic antimony compounds by Schmidt, *Ann.*, 421, 234 (1920).

(6) Fargher and Gray. *J. Pharmacol.*, 18, 364 (1921).

(7) All stibinic acids were prepared according to the general method of Dunning and Reid. THIS JOURNAL. 49, 2871 (1927).

Anal. Calcd. for $C_6H_4SbCl_2Br$: Sb, 34.93; Cl, 20.34; Br, 22.92. Found: Sb, 34.77; Cl, 20.22; Br. 23.10.

***p*-Bromophenyldiiodostibine.**—In order to obtain *p*-bromophenylstibine oxide, 35 g. of the dichloride was dissolved in 100 cc. of acetone and added slowly to a mixture prepared from 1000 cc. of water, 100 cc. of ammonia water and ice. The oxide which precipitated was filtered and air dried. To a solution of 12.5 g. of the oxide in 30 cc. of acetic acid, 14 cc. of hydriodic acid (sp. gr. 1.65) was added; *p*-bromophenyldiiodostibine precipitated as a yellow, crystalline solid. The material was washed thoroughly with water and dried in a desiccator; yield 22 g The iodide was recrystallized from absolute alcohol which contained a small amount of hydriodic acid; m. p. 124–125°.

Anal. Calcd. for $C_6H_4SbBrI_2$: Br, 15.03; I, 47.76. Found: Br, 15.25; I, 47.69.

Di-*p*-bromodiphenyliodostibine.—Di-*p*-bromodiphenylstibyl acetate was obtained in the following manner: 20 g. of p-bromophenylstibine oxide was placed in an Erlenmeyer flask and heated in a bath (145") in a stream of nitrogen for one hour. The pasty material was extracted with hot alcohol, the alcoholic solution filtered and the solvent removed. The oily tetra-p-bromotetraphenylstibyl oxide was treated with a small amount of acetic acid, whereupon it became crystalline through conversion of the stibyl oxide into the corresponding acetate; the yield of crude product was 17 g. In order to recrystallize the acetate, 10 g. of the material was dissolved in a mixture of 5 cc. of acetic acid, 10 cc. of benzene and 40 cc of heptane. The acetate melts at 134–135°.

To 4.9 g. of the acetate, dissolved in 20 cc. of hot acetic acid, there was added 2 cc. of hydriodic acid (sp. gr. 1.65). The mixture was cooled with ice and the crystalline di-*p*-bromodiphenyliodostibine removed by filtration. The iodide was thoroughly dried and then extracted in a Soxhlet apparatus with 150 cc. of petroleum ether (30–60°). The petroleum ether solution was decanted from the oily impurity which adhered to the sides of the extraction flask. The iodide, which separated from the cold solution, was recrystallized from heptane; m. p. 73–74'. The material is quite soluble in alcohol and benzene.

Anal. Calcd. for $C_{12}H_8SbBr_2I$: Sb, 21.72; Br, 28.51; I, 22.64. Found: Sb, 21.60; Br, 28.76; I, 22.64.

Tetra-*p*-bromotetraphenyldistibyl.—A solution of 4 g. of di-*p*-bromodiphenyliodostibine in 50 cc. of absolute alcohol and 2.5 g. of sodium hypophosphite, dissolved in 4 cc. of water and 4 cc. of alcohol, was poured into a free-radical bulb and after twelve hours the liquid decanted from the tan colored, crystalline precipitate. The product was washed twice with a mixture of 25 cc. of alcohol and 2 cc. of water, twice with absolute alcohol, twice with 20 cc. of hot xylene and finally with petroleum ether (30–60°). The product was dried under diminished pressure in a bath at 60° and isolated in a carbon dioxide atmosphere. The light greenish-yellow distibyl melted with decomposition at 211–213° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{16}Sb_2Br_4$: Sb, 28.08; Br, 36 85 Found: Sb, 27.95; Br, 36.83.

Dissolved in bromobenzene 1.272 g. of the distibyl absorbed 34 cc. (N. T. P.) of oxygen in one minute; calcd. absorption, 33 cc.

Di-*p*-tolyliodostibine.—To 400 g. of crude p-tolylstibinic acid, dissolved in 800 cc. of warm concd. hydrochloric acid, 800 cc. of water was added and the cold mixture filtered. The filtrate was diluted further with water until it became turbid. Sulfur dioxide was passed into the solution for a few minutes and after the removal of the gum the filtrate was cooled with ice and saturated with sulfur dioxide; yield 150 g. of practically colorless, crystalline *p*-tolyldichlorostibine; m. p. 89–92°.[8]

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(8) Hasenbäumer, *Ber.*, 81, 2914 (1898).

The dichlorostibine was dissolved in acetone and treated with ammonia water. whereupon p-tolylstibine oxide was obtained. The latter was washed with acetone and dried. *p*-Tolylstibine oxide was heated in a bath (100°) for two hours in order to convert it into tetra-*p*-tolylstibyl oxide. The crude oxide was extracted with hot alcohol. After recrystallization from alcohol the oxide melted at 101°.

Anal. Calcd. for $C_{28}H_{28}OSb_2$: Sb, 38.57. Found: Sb, 39.04.

In order to obtain di-*p*-tolylstibyl acetate, tetra-*p*-tolylstibyl oxide was dissolved in hot acetic acid. The acetate separated in crystalline form when the solution cooled; after recrystallization from heptane the acetate melted at 122–123°.

Anal. Calcd. for $C_{16}H_{17}O_2Sb$: Sb, 33.55. Found: Sb, 33.07.

To 10 g. of di-p-tolylstibyl acetate, dissolved in 50 cc. of acetic acid, 20 cc. of constant boiling hydriodic acid, diluted with 20 cc. of water, was added. The crude di-*p*-tolyliodostibine was washed free from hydriodic acid and extracted with petroleum ether; m. p. after recrystallization from absolute alcohol, 76–78°.[9]

Anal. Calcd. for $C_{14}H_{14}SbI$: Sb, 28.26; I, 29.46. Found: Sb, 28.23; I, 29.30.

Tetra-*p*-tolyldistibyl.—A solution, prepared from 3.5 g. of di-*p*-tolyliodostibine and 60 cc. of absolute alcohol, was poured into a free radical apparatus. There was added 2.5 g. of sodium hypophosphite, dissolved in 5 cc. of water and 20 cc. of alcohol. After twelve hours the supernatant liquid was decanted from the pale greenish-yellow crystals, the material washed several times with 90% alcohol and then with absolute alcohol. The product was isolated in a carbon dioxide atmosphere; m. p. 155–157° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{28}H_{28}Sb_2$: Sb, 40.07. Found: Sb, 39.50.

Dissolved in bromobenzene 0.917 g. of the distibyl absorbed 40 cc. (N. T. P.) of oxygen in three minutes; calcd. absorption 34 cc.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

The determinations were made in benzene by the Menzies method. A current of dry nitrogen was passed over the top of the apparatus during the determinations

Concn., %	ΔT, °C.	Mol. wt. found	Mol. wt. calcd. for $R_2Sb–SbR_2$
1.48	0.0766	621	607
2.44	.1250	627	
3.29	.1744	607	
4.32	.2248	619	

Di-α-naphthyliodostibine.—Two hundred grams of crude, dry α-naphthylstibinic acid[10] was dissolved in 500 cc. of cold hydrochloric acid, 200 cc. of water added and the mixture stirred for some time. After the removal of a black by-product by filtration, the filtrate was shaken with 25 g. of charcoal for twelve hours, filtered and the filtrate centrifuged in order to separate a black oil. The clear filtrate was cooled with ice and saturated with sulfur dioxide; α-naphthyldichlorostibine separated in crystalline form. After recrystallization from heptane, the material melted at 105–106°. The chloride is very soluble in benzene and absolute alcohol.

Anal. Calcd. for $C_{12}H_7SbCl_2$: Sb, 38.08; Cl, 22.18. Found: Sb, 38.07; Cl, 21.95.

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(9) Goddard and Yarsley [*J. Chem. Soc.*, 719 (1928)] described a compound, m. p. 233°, as di-*p*-tolyliodostibine which they obtained from tri-*p*-tolylstibine di-iodide. The high melting point alone indicates that their substance must possess a different structure.

(10) Riddell and Basterfield, *Trans. Royal Soc. Canada*, Third Series, Vol. XXIII, Part 1, Section III, p 48 (1929)

The dichlorostibine was hydrolyzed in the manner described above and 25 g. of the crude a-naphthylstibine oxide was heated (bath temperature 105–110°) in a stream of nitrogen for forty-five minutes. The tetra-a-naphthylstibyl oxide formed was extracted from the pasty reaction mixture with acetone and the acetone removed. The oxide was dissolved in 35 cc. of acetic acid and 8 cc of constant boiling hydriodic acid was added. Yellow di-α-naphthyliodostibine separated as an oil which became crystalline when cooled and rubbed. The dry iodide was extracted with petroleum ether; m. p. 136–137°.

Anal. Calcd. for $C_{20}H_{14}SbI$: Sb, 24.22; I, 25.24. Found: Sb, 24.19; I, 25.22

Procedure for **the** Determination of Antimony.—Compounds in which both antimony and halogen were to be determined were analyzed by the method of Thompson and Oakdale.[11] However, if antimony only is to be estimated, decomposition of the organic material can be effected in five minutes according to the following procedure. The sample and 20 cc. of concd. sulfuric acid are boiled in a 300-cc. Kjeldahl flask. If the sample contains iodine, the latter must be removed at this stage by the addition of several 2-cc. portions of hydrogen peroxide. Perchloric acid (70%) is added, dropwise, until the solution becomes colorless; 1 cc. is usually sufficient. The mixture is boiled for five minutes longer, cooled and diluted with four times its own volume of water. The pentavalent antimony is reduced to the trivalent state by treatment of the solution with sulfur dioxide for a short time. After the solution has been heated on a water-bath for one hour, it is boiled for fifteen minutes to remove sulfur dioxide completely, transferred to a 500-cc. Erlenmeyer flask and 10 cc. of concd. hydrochloric acid added. It is then titrated, at 60°, with 0.1 N potassium bromate solution with the use of methyl orange as indicator.

Summary

The following antimony compounds, hitherto unknown, have been prepared in a pure state: p-bromophenyldichlorostibine, *p*-bromophenyldiiodostibine, di-p-bromodiphenylstibyl acetate, di-*p*-bromodiphenyliodostibine, tetra-p-bromotetraphenyldistibyl, tetra-p-tolylstibyl oxide, di-p-tolylstibyl acetate, di-*p*-tolylstibyl iodide, tetra-p-tolyldistibyl, α-naphthyldichlorostibine and di-a-naphthyliodostibine.

The distibyls possess properties similar to those of diarsyls.

A procedure for the determination of antimony is described.

ANN ARBOR, MICHIGAN

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[11] Thompson and Odkdaie, THIS JOURNAL, **52, 1109 (1930).**

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK & CO., INC.]

The Identity of Narceine with Pseudonarceine, its Dehydration and Structure

BY C. R. ADDINALL AND RANDOLPH T. MAJOR

The accepted formulation of narceine as a substituted phenyl benzyl ketone, $C_{23}H_{27}NO_8\cdot 3H_2O$, and the establishment of its identity with the pseudonarceine of Roser,[1] are due to the continued investigations of Freund and his collaborators.[2] The misleading differences in physical properties and physiological effect between opium narceine and that made from narcotine were shown[3] to be due to impurities which were only eliminated after long and careful purification. The formula, $C_{23}H_{29}NO_9\cdot 2H_2O$, advanced by Anderson[4] for narceine had been confirmed by the analyses of later workers[6] but Roser demonstrated that pseudonarceine, which he considered identical with natural narceine, had the formula $C_{23}H_{27}NO_8\cdot 3H_2O$. The establishment of the identity of pseudonarceine and naturally occurring narceine by Freund and Frankforter through the analysis of their salts with alkali metals proved the latter to be derived from a substance having the formula $C_{23}H_{27}NO_8$. Determination of the water of crystallization content of natural narceine showed the presence of three molecules of water, two of which were lost with ease, the third only with great difficulty. On account of this and the extremely hygroscopic nature of the dried material the composition of the fully dried narceine is in doubt From his work on the color reaction of sodium nitroprusside[6] with narceine, Zwikker[7] came to the conclusion that the $—CH_2CO$ grouping of desoxybenzoin is not present in narceine, but that a ring closure between the $—CH_2$ and a neighboring $—NMe_2$ has occurred whereby the —CO group is attached directly to two rings and is therefore no longer reactive. Narceine would then have the same ring structure as the parent substance Narcotine. The fluorescence of narceine under ultraviolet irradiation and the conclusion of Moir[8] that fluorescence may occur in all cases where two rings are joined at two places by two groups of almost any sort, offers some support for this assumption. Failure on our part to reduce narceine to hydronarceine[9] by catalytic hydrogenation, to carry out a benzylidene condensation[10] and to isolate the alkyl narceines, together with lack of success in the

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(1) Roser, *Ann.*. **247**, 187 (1888).

(2) Freund and Frankforter, *ibid.*, 277, 20 (1893); Freund and Michaels, *ibid.*, 286, 248 (1895); Freund, *Ber.*, 40, 194 (1907); Freund and Oppenheim, *ibid.*, 42, 1084 (1909).

(3) Schroeder, *Arch. exptl. Path. Pharmakol.*, 17, 138 (1883).

(4) Anderson, *Ann.*, 86, 179 (1853).

(5) Hesse, *ibid.*, **129**, 250 (1864); Beckett and Wright, *J. Chem. Soc.*, **28**, 699 (1875); Claus and Meixner, *J. prakt. Chem.*, [2] **37**, 1 (1888).

(6) Bela von Bitto, *Ann.*, 269, 377 (1892).

(7) Zwikker, *Pharm. Weekblad.*, 66, 481 (1929).

(8) Moir, *Trans Roy. Soc. S. Africa*, **12**, *Pt.* 2, 45 (1924)

(9) Max and Michel Polonovski, *Bull. soc. chim.*, 49, 541 (1931)

(10) Knoevenagel and Weissgerher, *Bcv.*, **25**, 442 (1893)

repetition of Freund's narcindonine preparations[11] so vital to the conception of narceine as a highly substituted desoxybenzoin, coupled with the uncertain nature of dried narceine and the recent doubts as to its structure, led to the undertaking of the preparation of pure narceines from opium and narcotine sources, their dehydration and the investigation of the possibility of a modified formula for narceine.

Narceine was prepared from narcotine by the methods of Roser and of Hope and Robinson.[12] After careful purification these narceines and that from opium were converted into their sodium salts, hydrochlorides, chloroplatinates and picrates and the identity of these derivatives was established by melting point determinations. Further evidence as to absolute identity was afforded by examination of the carefully purified narceines by ultraviolet radiation. Polarimetric measurements showed all three narceines alike to be optically inactive.

Previous attempts to dehydrate narceine and to analyze the water-free material had always failed. Not only is the dried material extremely hygroscopic but some decomposition takes place, causing the resulting dried narceine to be variable in composition. By combining the drying process and the analysis a satisfactory series of analyses for the dried material was obtained.[13] These results, in conjunction with the water of crystallization determinations made by a macro method, gave a completely satisfactory analysis of narceine for carbon, hydrogen and water of crystallization. These analytical results give further support to the proof of the absolute identity of narceine prepared from narcotine with that found among the products extracted by the established trade procedures from the gum of the opium poppy along with morphine and narcotine.

It would therefore seem that air-dried narceine has the constitution $C_{23}H_{27}NO_8{\cdot}3H_2O$ and that, always provided that the drying temperature does not exceed 110° and is not prolonged more than two hours, the sample not being exposed to oxidation during this period, the water of crystallization can be removed quantitatively without the decomposition of the dry material, which has then the empirical formula $C_{23}H_{27}NO_8$ (I) precluding the possibility of the structure of narceine being represented by any structural formulation involving the empirical formula $C_{23}H_{29}NO_9$. Since all of the substituent groups, *i. e.*, 3(OMe), COOH, CH_2O_2, C_2H_4-NMe_2 are well established, only the validity of the supposed —$COCH_2$— grouping remains doubtful in the present recognized structural formulation.

Narceonic acid (II) prepared by a modification of the method of Freund[14] was converted into dihydronarceonic acid by catalytic hydrogenation. Treatment of the methyl ester of this saturated acid with MeMgI in an

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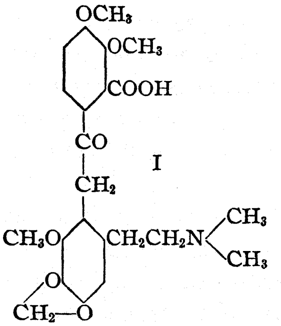
[11] Freund and Oppenheim, *Ber.*, **42**, 1084 (1909).

[12] Hope and Robinson, *J. Chem. Soc.*, *105*, 2100 (1914).

[13] Hayman, *Ind. Eng. Chem.*, *Anal. Ed.*, *4*, 256 (1932).

[14] Freund. *Ann.*, **277**, 66 *(1893)*.



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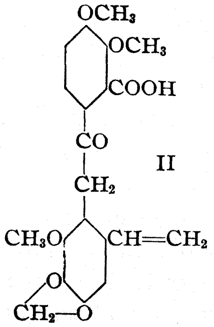

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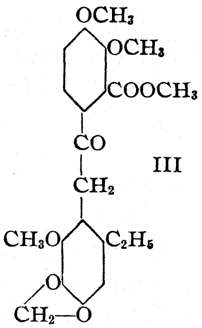

III

apparatus for determining both the quantity of gas evolved and the amount of reagent consumed[15] showed that it contained no active hydrogen and so afforded evidence against the assumption of OH groups in the narceine molecule. This evidence was confirmed by the failure of many attempts to methoxylate narceine and its derivatives. The formulation of narceine as a highly substituted desoxybenzoin and the erroneous claims of early workers[16] led to many fruitless efforts to isolate alkyl narceines and its derivatives. The bromination of this methyl ester with bromine in chloroform gave an interesting monobromide $C_{22}H_{23}O_8Br$ which may contain a bromine atom in the only unoccupied position of the cotarnine half of the molecule. The ease of substitution in this position has already been noted.[17]

Through ring formation with the COOH group the addition of $HONH_2$ and $PhNHNH_2$ to narceine yields oxime and phenylhydrazone anhydrides. The condensation of $MeONH_2$ with narceine to give the simple addition compound $C_{24}H_{30}N_2O_8$ without further internal rearrangement affords further evidence for the accepted $—COCH_2—$ formulation.

We wish to thank Mr. Douglas F. Hayman of this Laboratory for the microanalyses recorded in this paper and also Professor E. P. Kohler for his kindness in carrying out the active hydrogen determination.

Experimental Part

Preparation of Pure Narceine from Opium and Synthetic Material

Opium Narceine.—Commercial narceine recovered from the mother liquors from the preparation of morphine hydrochloride usually contains small amounts of acid and other impurities from which it is freed with difficulty.[18] The impure factory narceine was dissolved in dilute hydrochloric acid and then made slightly alkaline with ammonia. The alkaline solution was digested on the steam-bath and then allowed to cool. After crystallization the filtered material was dissolved in a minimum of hot 95% alcohol and after dilution to 50% with distilled water the solution was cooled. The resulting fine prismatic needles were recrystallized from hot water.

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(15) Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

(16) Claus and Ritzefeld, *Ber.*, 18, 1669 (1888); Tambach and Jaeger, Ann. 349, 185 (1906); Knoll and Co., *Friedländer*, VIII, 1164,1166.

(17) Freund and Fleischer, *Ber.*, 46, 1171 (1912).

(18) Merck, *Chem.-Ztg.*, 13, 525 (1889).

Narceine (Roser).—Narcotine, recrystallized from acetone, was digested with an excess of methyl iodide for four hours. The crude gum was freed from methyl iodide by heating *in vacuo* and the resulting dry amorphous yellow powder was digested with freshly prepared silver chloride in water. The addition product gradually went into solution and the quaternary ammonium chloride was filtered free from the silver iodide formed. On treatment with potassium hydroxide and heating on a steam-bath crude narceine separated out.

Narceine (Hope and Robinson).—To 60 g. of recrystallized narcotine was added 21 g. of redistilled dimethyl sulfate in the cold. The mixture was shaken, warmed on steam-bath and stood overnight in a stopperec! 250-cc. Erlenmeyer flask. Benzene was added to ensure contact, and after refluxing for a time, was removed. Water was added and the flask was warmed until solution was effected. On adding potassium hydroxide to slight alkalinity and heating, crude narceine was formed.

The crude synthetic narceines were dissolved in dilute hydrochloric acid and precipitated with ammonia. They were then recrystallized from 50% alcohol until yellowness was absent from the mother liquors. The coloration present was due to a brown water-soluble oil which was soluble also in alcohol and alkali and which could be removed from neutral solutions by boiling with norite. The colorless material was recrystallized from boiling water and the filtered cakes were dried by exposure to the air in a dust proof box.

All three materials melted between 171–173°. The opium and Roser samples were unchanged under ultraviolet radiation whereas all Hope and Robinson samples showed a green fluorescence. Analyses for the two former corresponded to $C_{23}H_{27}NO_8 \cdot 2H_2O$ and to $C_{23}H_{27}NO_8 \cdot 2.5H_2O$ for the latter material. The narceines were treated with freshly prepared 33% sodium hydroxide, heated on the steam-bath and the hard lumps formed were broken up with a glass rod. After digestion and filtration through a sintered glass funnel the residue was ground up to a fine paste which was returned to fresh 33% sodium hydroxide and was redigested. In this way a clear solution was obtained which gave a crystalline material on cooling. After filtration and washing with cold ethanol the solid was dissolved in hot ethyl alcohol and on cooling ether was added. Large white crystals were formed which were redissolved in hot ethyl alcohol and recrystallized.

In some of the preparations a red color appeared on dissolving the crude sodium salt in ethyl alcohol with heating. This color formation was accelerated by the addition of norite. By converting the crude sodium salt into narceine with dilute acetic acid, recrystallizing the narceine from water and treating with 33% sodium hydroxide, a sodium salt was formed which gave a colorless alcoholic solution.

The sodium salts, all melting at 162–163°, melting point unchanged on mixing, were dissolved in hot distilled water and carbon dioxide was passed through the dilute solution. The cold solution containing a semi-solid crystalline network was filtered, the narceine was shaken up in cold water and washed three times by decantation. The narceines so formed were recrystallized from water. The samples were then placed in an air-drier consisting of a box with a sliding front and a back covered with good grade fine-meshed cheese cloth. The material was dried for forty-eight hours and after being finely ground was dried again for twenty-four. hours. Samples were then bottled in vials with screw caps, the inner cork lining being covered with waxed paper. All samples had m. p. 176–178°.

ANALYSES OF AIR-DRIED NARCEINES

Calculated for $C_{23}H_{27}NO_8 \cdot 3H_2O$		C, 55 31		H, 6.61	
Found:	Opium narceine	55.75	55.72	6.28	6.30
	Roser narceine	55.42	55.57	6.52	6.57
	Hope–Robinson narceine	55.19	55.26	6.71	6.69

Quantitative Determination of the Water of Crystallization.—Nitrogen freed from oxygen and moisture by passage through concd. sulfuric acid, over hot copper shavings and through a U-tube packed with dehydrite was passed slowly over a weighed sample of narceine contained in a U-tube placed in a drying oven for two hours at 103–105°. The moisture absorbed by the nitrogen was removed by passage through a weighed U-tube containing dehydrite which was guarded from the air by a second similar tube. The whole train terminated in a U-tube of concd. sulfuric acid acting as a bubble counter and included a deep sulfuric acid T-safety valve between the supply tank and the first sulfuric acid wash bottle.

Narceine	Sample, g.	*Water* lost, g.	Water recovered, g.	% H_2O (Calcd. for $3H_2O$, 10.82)
Opium	1.9043	0.2021	0.2025	10.61
	1.6147	.1730	.1737	10.73
Roser	2.8440	.3036	.3038	10.68
Hope–Robinson	1.2016	.1292	.1296	10.77

In the case of the Hope–Robinson material advantage was taken of the previous results and the sample was purified still further by reconversion into the sodium salt and back again to narceine—both materials being recrystallized from water. The heating was continued for three and one-half hours at 101–102°.

Analysis of Narceine Freed from Water of Crystallization.—Although excellent results for $3H_2O$ were obtained by the above macro-analysis, the satisfactory analysis of the dried material was found to be impossible by the usual procedure. Dehydration of the air-dried material weighed out in a platinum boat placed in a combustion tube in the same manner as for a regular carbon and hydrogen determination was carried out by the passage of preheated dry nitrogen over the sample heated to 100–105° by a Pregl heating block. The absorption tubes were then attached and the combustion was completed in the usual manner. The results of the analysis of the dried material were excellent and these in conjunction with the determinations of the water of crystallization by the macro method give a completely satisfactory and definite determination of narceine for carbon, hydrogen and water of crystallization. The Hope–Robinson material (calcd. for $C_{23}H_{27}NO_8 \cdot 3H_2O$: C, 55.31; H, 5.61; H_2O, 10.82; N, 2.80. Found: C, 55.26; H, 6.69; H_2O, 10.77; N, 2.85) was used throughout the analyses.

Anal. Calcd. for $C_{23}H_{27}NO_8$: C, 62.02; H, 6.07. Found: C, 62.09, 62.26; H, 5.73, 5.75.

The Melting Points of Narceines and their Derivatives.—Narceine dissolves in a solution of hydrochloric acid in methanol. The solution deposits crystals with a composition $C_{22}H_{27}NO_8 \cdot HCl \cdot CH_3OH$. On heating for a short time at 100° the methanol is totally eliminated with the formation of $C_{23}H_{27}NO_8 \cdot HCl$. This hydrochloride when dissolved in 16% hydrochloric acid and warmed at 70–80° with chloroplatinic acid yields a chloroplatinate. Narceine forms a distinctive picrate[19] by mixing aqueous solutions of picric acid and narceine. The opium, Roser and Hope–Robinson narceines and their derivatives prepared according to the above procedures have the following melting points: narceine, $C_{23}H_{27}NO_8 \cdot 3H_2O$, m. p. 176–177°, liquefying to an almost colorless melt, decomposing with evolution of gas between 176 and 178°. Sodium narceinate, $C_{23}H_{26}NO_8Na$, m. p. 162.163°. Narceine hydrochloride, $C_{23}H_{27}NO_8 \cdot HCl$, m. p. 192–193°. Narceine chloroplatinate $(C_{22}H_{27}NO_8 \cdot HCl)_2PtCl_4$, m. p. 195–196° (decompn.). Narceine picrate, m. p. 195°. Mixed melting point determinations showed no depression.

The Melting Point of Water-Free Narceine, $C_{23}H_{27}NO_8$.—In view of the difficulties

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(19) Maplethorpe and Evers, *Pharm. J.*, 115, 137 (1926).

found in completely drying narceine and preventing the extremely hygroscopic material from changing its composition by absorption of water from the air, a current of pure dry nitrogen was passed through capillary tubes containing narceine. The samples were introduced into the middle of the capillary tubes and were enclosed by the regenerating block of the Pregl outfit. They were submitted to two hours of drying in the current of dry nitrogen at 105–110°. The capillary tubes were then sealed by a point flame and after cooling the samples were shaken down to one end Opium, Roser and Hope–Robinson narceine samples were used. Samples previous to drying, $C_{23}H_{27}NO_8{\cdot}3H_2O$, m. p. 176–178°; samples after drying, $C_{23}H_{27}NO_8$, m. p. 137–138° (to a water white melt). Merck[18] gives 170–171" for the melting point of the hydrated base while Hesse stated that the anhydrous material melted at 140.5°.[20]

Fluorescence Phenomena.—The identity of the various samples of narceine was investigated by examination of the carefully purified samples by means of ultraviolet radiation provided by a Hanovia Universal quartz-mercury arc lamp provided with a filter screen. The filter is of special composition glass which absorbs the visible light and permits the passage of the invisible–consisting largely of the long wave ultraviolet—but *including a narrow band in the extreme violet, just within the border of visibility.* With this extreme violet visible light in mind comparison of various samples was made with the results recorded by Boyle and Fabre[21] who used a ray 365.0 Hg provided by a mercury arc lamp with a thick nickel oxide screen. Most glasses fluoresce and since paper "fluoresces beautifully" under the Hanovia lamp, the air-dried powdered samples were viewed on strips of densely black dull matte paper (from a Bausch and Lomb catalog) which showed no fluorescence whatsoever. Boyle and Fabre had found narcotine and narceine to fluoresce with a clear violet tinge. Examination of narcotine and the three narceines showed them to act alike and to exhibit a very faint purplish tinge. Whatever may be the interpretation of the variation in the tints observed by us as compared with those reported by Boyle and Fabre, it was established that no difference in fluorescence phenomena exists between the various samples of narceine. When insufficiently purified samples are observed such differences are apparent but the green fluorescence previously exhibited by an impure Hope–Robinson preparation was evidently not due to traces of narcotine. The discrepancy in the descriptions of different workers of the appearance of fluorescence, the misty violet tinge of the mercury light as seen through a Wood's glass filter and the disturbing effects of traces of impurities have recently been the subject of comment by Grant.[22]

Optical Activity.—The three narceines were identical in their behavior, showing no optical activity in either acid or alkaline solution. These findings are contrary to those of Bouchardat and Bondet,[23] who were probably using slightly impure material, and in agreement with those of Hesse.[24]

Narceonic Acid, $C_{21}H_{20}O_8$ (@).—Fifty grams of narceine was heated to a clear solution with 100 cc. of 4% sodium hydroxide, and 12.5 g. of dimethyl sulfate was weighed into a cold solution. The mixture was gently heated in a glass-stoppered flask for two hours on the steam-bath. An excess of concentrated hydrochloric acid was added and the digestion continued as long as the solution deposited crystalline material. After the mixture had cooled and stood overnight, the crude solid was filtered; yield 50 g. of a white crystalline narceine methochloride, m. p. 243°. A suspension of 20 g. of this crude methochloride in 150 cc. of absolute alcohol was refluxed in the hood and 40 cc. of 33% potassium hydroxide was added. The refluxing was continued for one

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(20) Hesse, *Ann.*, **129**, 250 (1864).

(21) Boyle and Fabre, *Compt. rend.*, 178, 2181–3 (1924).

(22) Julius Grant, *Chemist and Druggist*, *116*, 421 (1932)

(23) Bouchardat and Bondet, *J. Pharm. chim.*, [3] *23*, 292 (1853).

(24) Hesse, *Ann.*, **176**, 199 (1875).

and one-half hours until the emission of trimethylamine ceased. The clear orange solution was filtered and diluted with water. This dilute alkaline solution was added slowly with efficient stirring to about **1.5** liters of dilute hydrochloric acid. The pure white precipitate was filtered and washed. After air-drying the crude material weighed **16** g. and melted at 217°; recrystallized from butanol, m. p. **217".**

Dihydronarceonic Acid, $C_{21}H_{22}O_8$.—Ten grams of narceonic acid **(0.025** mole) was heated to a clear solution with **150** cc. of methanol and **15** cc. of dioxane. To this clear warm solution in a magnesium citrate bottle was added **0.2** g. of platinum catalyst. On hydrogenation **0.025** mole of hydrogen were absorbed in about two minutes. After filtration through a sintered glass funnel, the clear solution was added to a large excess of cold distilled water. The white precipitate was recrystallized from hot methanol, m. p. 197–198°; yield **10** g.

Anal. Calcd. for $C_{21}H_{22}O_8$: C, **62.69;** H, **5.47.** Found: C, **62.53;** H, **5.28.**

Esters of Narceonic Acid.—Though attempts to esterify narceonic acid by refluxing alcoholic solutions with dry hydrochloric acid failed, the esters were formed by refluxing the silver salt, $C_{21}H_9O_8Ag$, with methyl and ethyl iodides. The resulting products when recrystallized from their respective alcohols yielded methyl narceonate, m. p. **155°**, and ethyl narceonate, m. p. **139–140°.**

Anal. Calcd. for $C_{22}H_{22}O_8$: C, **63.77;** H, **5.31.** Found: C, **63.48;** H, 5.14.

Anal. Calcd. for $C_{23}H_{24}O_8$: C, **64.48;** H, **5.61.** Found: *C*, **64.50;** H, 5.80.

Methyl Diydronarceonate (III).—By refluxing dihydronarceonic acid dissolved in methanol containing about **4%** of hydrochloric acid esterification took place readily. The ester was insoluble and crystallized out during the operation. The material held tenaciously a yellow coloration but gave a snow-white product on recrystallization from benzene, m. p. **155'.**

Anal. Calcd. for $C_{22}H_{24}O_8$: C. **63 46;** H, **5.77.** Found: C, 63.25; H, **5.70.**

When **0.3** millimole of III was added to **6** cc. of a solution of MeMgI in isoamyl ether,[25] about half of the material dissolved in the cold without giving off a trace of gas. The substance, therefore, contained no active hydrogen. More dissolved on heating but efforts to get a complete solution were unsuccessful. It was estimated that one mole of the substance reacted with three moles of the reagent without giving off any gas.

Bromination of 111.—Treatment of a chloroform solution of III with bromine in chloroform, removal of the chloroform and recrystallization of the product from methanol gave $C_{22}H_{23}O_8Br$ containing methanol of crystallization which was removed with difficulty, it being necessary to dry at 80° for one and one-half hours and then at **120"** for two hours to yield *methyl dihydronarceonate monobromide,* m. p. 189°.

Anal. Calcd. for $C_{23}H_{23}O_8Br$: C, **53.33;** H, **4.65;** Br, **16.2.** Found: C, **53.37;** H, **4.54;** Br. **16.6.**

Narceine Methoxime.—To a solution of **1** g. of narceine in **50** cc of methanol was added 0.2 g. of $MeONH_2$. The mixture was heated in a bomb tube for **70–80** hours at **118"** and then concentrated by evaporation on a steam-bath. The product crystallized out in good yields. It was crystallized from methanol and washed with ether, the crystals disintegrating to a fine crystalline powder which was dried at **100"** for three hours, m. p. 190°.

Anal. Calcd. for $C_{24}H_{30}N_2O_8$: C, **60.76;** H, **6.33.** Found: C, **60.54;** H, **6.29.**

Summary

1. The identity of opium narceine with that obtained by the conversion of narcotine methyl iodide, chloride and methosulfate has been con-

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(25) **Kohler.** Stone and **Fuson,** THIS JOURNAL, **49, 3181** (1927).

firmed by comparison of the physical properties of carefully purified material.

2. The formulation of narceine as $C_{23}H_{27}NO_8 \cdot 3H_2O$ has been definitely established by quantitative determination of the water of crystallization content and analyses of the dehydrated material.

3. Dihydronarceonic acid, its methyl ester and the methyl and ethyl esters of narceonic acid have been prepared.

4. Although attempts to alkylate the methylene group and to effect the reduction of the CO group by catalytic hydrogenation were unsuccessful, the lack of active hydrogen in methyl dihydronarceonate, its behavior on bromination and the formation of narceine methoxime confirm the formulation of narceine as a highly substituted desoxybenzoin.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL WORKS]

The Reaction between Acid Chlorides and Ethers in the Presence of Zinc Chloride

BY L. P. KYRIDES

Descudé[1] reported that on mixing acetyl chloride and anhydrous ethyl ether with a sufficiently large amount of zinc chloride a violent reaction took place immediately which needed to be kept under control by means of external cooling. On working up the reaction mixture he obtained ethyl acetate and ethyl chloride in yields approximating 90 and 67%, respectively, on acetyl chloride, based on the equation

$$CH_3COCl + (C_2H_5)_2O \longrightarrow CH_3CO_2C_2H_5 + C_2H_5Cl$$

The author, furthermore, makes the statement that "the yields are almost theoretical."

Wedekind and Hauessermann[2] obtained a 50% yield of ethyl benzoate from benzoyl chloride and excess of ether in presence of large amounts of sublimed ferric chloride.

Recently H. W. Underwood, Jr., has extended the study of this reaction, stressing the catalytic action of zinc chloride. He and Wakeman[3] have refluxed the acid chlorides mixed with a slight excess of anhydrous ethers in presence of relatively substantial amounts of zinc chloride and isolated the corresponding esters in some instances in as high as 79% of the theoretical yield.

The amount of alkyl chlorides isolated by Underwood and Toone[4] was far from that which is required by Descudé's equation. The authors, in

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[1] Descudé, Compt. rend., **132**, 1129 (1901).

[2] Wedekind and Haussermann, *Ber.*, **34**, 2081 (1901).

[3] Underwood and Wakeman, THIS JOURNAL, **52**, 387 (1930).

[4] Underwood and Toone, *ibid.*, **52**, 391 (1930).

discussing the action of zinc chloride on ethers, indicate that the ether is decomposed into alcohol and an alkylene. If an acid chloride is present it reacts with the alcohol to form an ester, while the liberated hydrochloric acid reacts with some alcohol to produce the alkyl chloride Accordingly, based on the mechanism of the reaction as outlined, the amount of the ester formed cannot possibly exceed that which is equivalent to the unsaturated hydrocarbon; while the alkyl chloride, being a by-product, can be formed only in relatively small amounts. The authors isolated the alkyl chlorides in yields not much over 30% of the theoretical.

Because of the discrepancy between Descudé's statement and the results obtained by Underwood and his co-workers, it seems desirable that a quantitative isolation of the products of the reaction should be made.

In our case, where we used a mere trace of zinc chloride, the reaction between benzoyl chloride and ethyl ether gave results substantially as indicated in the equation given above.

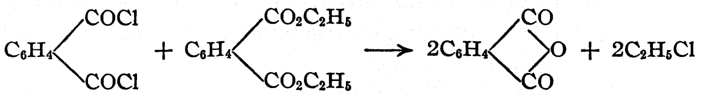
In the case of other ethers, the amounts of alkyl chlorides isolated will be less, since these chlorides have a greater tendency to decompose into an alkylene and hydrochloric acid.

In the case of o-phthalyl chloride, Underwood and Wakeman observed that it reacts with ethyl ether in the presence of zinc chloride to form large amounts of phthalic anhydride together with a small amount of diethyl phthalate, and they conclude that the results "indicate that diethyl phthalate may be transformed into phthalic anhydride by zinc chloride."[5]

In order to avoid any side reactions which might be induced by the catalyst, we have used only traces of it in the reactions studied.

We have observed that the chlorides of the monocarboxylic acids in reaction with ether in the presence of traces of zinc chloride require higher temperatures and longer time for completion than phthalyl chloride. With low boiling acid chlorides such as butyryl chloride, the reaction is hardly noticeable even at boiling temperature. Higher boiling acid chlorides, such as lauryl and benzoyl chlorides, show a distinct rate of reaction above 140°. By slowly dropping ether into benzoyl chloride containing traces of zinc chloride above 140°, we were able to isolate ethyl benzoate and ethyl chloride in good yields following the equation given above.

In the case of o-phthalyl chloride, the reaction product does not contain any appreciable amount of the expected diethyl phthalate, due to the fact that the latter reacts readily with phthalyl chloride in the presence of zinc chloride to give two moles of ethyl chloride as follows



$$C_6H_4\left\langle {COCl \atop COCl} \right. + C_6H_4\left\langle {CO_2C_2H_5 \atop CO_2C_2H_5} \right. \longrightarrow 2C_6H_4\left\langle {CO \atop CO} \right\rangle O + 2C_2H_5Cl$$

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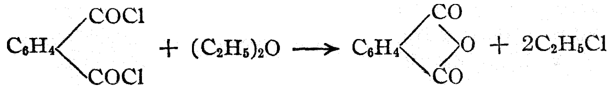
(5) See also Underwood and Baril, THIS JOURNAL, 52, 396 (1930).

so that the final result of the reaction may be expressed by the equation



$$C_6H_4(COCl)_2 + (C_2H_5)_2O \longrightarrow C_6H_4(CO)_2O + 2C_2H_5Cl$$

Experimental

(1) Reaction between Benzoyl Chloride and Ethyl Ether.—One hundred and fifty grams of benzoyl chloride (1.06 g. moles) and 0.5 g. of technical anhydrous zinc chloride were charged into a three-necked, 500-cc. flask carrying a very efficient spiral reflux condenser, dropping funnel and thermometer. The flask was heated and the reaction temperature maintained at about 150°; 90 g. (1.21 g. moles) of freshly distilled ethyl ether was dropped in over a period of about ten hours at such a rate that the temperature could be maintained at the point indicated. Toward the end of the addition of the ether, the reaction temperature was raised to 170°. The reaction gases were cooled through the reflux spiral condenser, which was kept at the boiling point of ethyl chloride by running cold water, and, after bubbling through water, were condensed by means of a spiral condenser kept at 0° and collected in a receiver cooled at about —5°.

The liquid which was collected was fractionated carefully from small amounts of ethyl ether through an efficient spiral condenser maintained at 12° by running cold water. In this manner 54 g. of ethyl chloride boiling at 12° (a few drops up to 16°) was collected. This is equivalent to 78.0% yield.

The residue from the distillation was fractionated directly *in vacuo:* 146.5 g. of colorless ethyl benzoate was obtained boiling at 96 to 98° at about 20 mm. This is equivalent to a 91.5% yield from benzoyl chloride. The product was free from any odor of benzoyl chloride and on analysis showed minute traces only of chlorine.

The ester, upon fractionation at atmospheric pressure, boiled to the extent of 97% at 208°.

In the above reaction a small amount of uncondensed combustible gas escaped, which was undoubtedly ethylene. Allowing for unavoidable losses in the handling of ethyl chloride, it appears evident that Descudé's equation is substantially correct.

Lauryl chloride reacts similarly but very slowly with ether at its boiling point.

(2) Phthalyl Chloride and Ethyl Ether.—Two hundred and fifty grams (1.18 g. moles) of phthalyl chloride (analyzing 96%) and 0.4 g. of zinc chloride were charged into a three-necked flask (connected as under benzoyl chloride). The mixture was heated at 110° in the beginning and the temperature gradually raised to 170° as the reaction progressed, in order to avoid crystallization of the phthalic anhydride; 110 g. (1.48 g. moles) of ethyl ether was dropped in over a period of three hours. The ethyl chloride formed was fractionated in the presence of water through a spiral condenser maintained at 12°; 137 g. of distillate was obtained boiling up to 20°. This was redistilled and 122 g. of liquid was collected boiling at 12° (a few drops up to 14'). The latter amount is equivalent to an 80% yield on phthalyl chloride assuming that two molecules of ethyl chloride are formed per mole of phthalyl chloride and ether.

(3) Phthalyl Chloride and Isopropyl Ether.—Two hundred grams (0 946 g. mole) of phthalyl chloride (96%) and 0.5 g. of zinc chloride were heated at 130 to 140° at first and then gradually raised to 170° during the reaction. The reflux spiral condenser in this case was cooled by a slow current of running water so that any isopropyl chloride formed would distil over. The reaction products were cooled with ice water; 110 g. (1.08 g. moles) of isopropyl ether (freshly distilled) was dropped in within six hours. In this case it was observed that a considerable amount of gas, which was undoubtedly propylene, escaped condensation. In order to eliminate the presence of any hydrochloric acid in the condensate, even after bubbling the gases through warm water be-

fore condensation, the condensate was shaken with cold water and distilled. The wet distillate was dried over calcium chloride and refractionated. The isopropyl chloride obtained in this manner weighed 92 g., which is equivalent to a yield of 62% from phthalyl chloride. The low yield of chloride is explained by the fact that isopropyl chloride readily undergoes decomposition to propylene and hydrochloric acid.

Summary

The chlorides of high boiling monocarboxylic acids react with ethyl ether in the presence of traces of zinc chloride. With benzoyl chloride, ethyl chloride and the ester are obtained in good yield.

Equimolecular amounts of o-phthalyl chloride and ethyl ether react to give phthalic anhydride and approximately two molecules of ethyl chloride.

o-Phthalyl chloride and isopropyl ether react similarly to give phthalic anhydride and isopropyl chloride, but in this case larger amounts of propylene are formed as a by-product.

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The Halogenation of Meta-Diphenylbenzene. I. The Monochloro and Monobromo Derivatives

BY WALTER A. COOK AND KATHRYN HARTKOFF COOK

In the commercial manufacture of biphenyl from benzene, considerable quantities of the meta and para isomeric diphenylbenzenes are formed as by-products, the meta isomer predominating. Very little is reported in the literature on derivatives of the latter hydrocarbon. Olgiati[1] described the monobromo and tetrabromo derivatives and others the trinitro and triamino derivatives.[2] Recently, Wardner and Lowy[3] reported the synthesis of the mononitro, the dinitro and related compounds. In no case, however, has sufficient experimental proof been advanced to establish completely the structures of the above-mentioned derivatives.

This paper is limited to an account of the monochloro and monobromo derivatives, their oxidation products, and their proof of structure. A later publication will describe the preparation and properties of the polychloro and polybromo derivatives. Further study of the applications of the monohalogen derivatives to the Grignard reaction and the synthesis of metallo organo compounds, including the mercury and arsenic types, has been planned, and work in that direction is being pursued in this Laboratory.

The authors acknowledge their great indebtedness to Mr. R. E. Bowman of Wilmington, Delaware, for the generous supply of purified *m*-diphenyl-

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(1) Olgiati. Ber., 27, 3385 (1894).

(2) Schultz and Schmidt, Ann., 203, 118 (1880).

(3) Wardner and Lowy. THIS JOURNAL, 64. 2510 (1932).

benzene, and for the frequent suggestions and aid given during the course of this investigation.

Experimental Part

Chlorination of *m*-Diphenylbenzene

4-Chloro-1,3-diphenylbenzene.—Fifty-four grams of *m*-diphenylbenzene and several nails freshly cleaned with hydrochloric acid were placed in a 250-cc. distilling flask and heated on a water-bath. After the material had liquefied, a slow stream of chlorine gas was introduced. Reaction occurred rather slowly and the introduction of gas was continued until the weight of the reaction mixture had increased to 20% excess over the theoretical quantity. The flask and contents were then set aside for several hours to ensure completion of the reaction, and the increase in weight of the contents of the flask again determined so as to ensure the required excess indicated above. The mixture was then dissolved in petroleum ether (30–60°) to remove a small quantity of insoluble material which had formed. After filtration and removal of solvent, a thick yellow oil remained. This on fractionation yielded 52.6 g. (84.2%) of a viscous almost colorless and odorless oil with a boiling range of 214–216° (4 mm.). Specific gravity, 25/25°, 1.1903; refractive index (n_D^{25}), 1.6564.[4]

Anal. Calcd. for $C_{18}H_{13}Cl$: Cl, 13.40. Found: Cl, 13.63.

Oxidation of Monochloro-*m*-diphenylbenzene.—Seven grams of the above oil was dissolved in sufficient glacial acetic acid so that none separated when cooled to room temperature. To this was added in small portions with frequent cooling of the reaction mixture, an 85% excess of CrO_3 over the theoretical quantity required for the oxidation of a phenyl group. It was allowed to stand for several hours at room temperature and poured into a large volume of cold water, whereupon a voluminous precipitate of the acid appeared. The pale yellow color of the resulting product was due to a small quantity of the unoxidized monochloro derivative contaminating the acid. A product of higher purity was obtained when a greater excess of CrO_3 was employed, but the yield was much lower than in the previous instance. Oxidation with potassium permanganate in acetic acid also gave a purer product but lower yield. Hence the contaminated product was dissolved in concentrated ammonium hydroxide and treated with a solution of manganous acid freshly prepared from manganese sulfate, potassium chlorate and nitric acid. On filtration, the flocculated manganese dioxide adsorbed the small quantity of oily monochlorodiphenylbenzene and the filtrate on acidifying with sulfuric acid yielded a voluminous white precipitate of the acid. The acid was removed by filtration, then redissolved in ammonium hydroxide, filtered and reprecipitated by the addition of sulfuric acid. The yield of the pure product was 3.5 g. (30%). Ordinary methods of purification of the contaminated acid by the use of solvents in place of the treatment with manganese dioxide require several recrystallizations with far less satisfactory yields due largely to increased mechanical losses. The melting point of the purified product was 208–209°.

Anal. Calcd. for $C_{13}H_9O_2Cl$: Cl, 15.25. Found: Cl, 15.18.

Silver Salt of the above Chlorophenylbenzoic Acid.—Two grams of the above acid was suspended in water and neutralized with 6 *N* ammonia. On addition of an equivalent of silver nitrate (aqueous solution), a heavy white precipitate formed. This was filtered on a Buchner funnel and then transferred to an amber desiccator; yield, 2.8 g. (theoretical, 2.9 g.). The moist silver salt turns pink on exposure to light and is soluble both in ammonium hydroxide and acids.

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(4) Crude m-diphenylbenzene can be chlorinated in the same way and the monochloro derivative obtained by a similar method of purification.

Methyl Ester of the above Chlorophenylbenzoic Acid.—One gram of the above silver salt was suspended in ether and treated with an equivalent of methyl iodide. After standing for several days in the dark the silver iodide was removed by filtration and the filtrate warmed to remove the solvent; yield, 0.5 g. of a yellow pungent oil; refractive index (n^{30}_{D}), 1.5952.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: Cl, 14.38. Found: Cl, 14.47.'

Benzyl Ester of the above Chlorophenylbenzoic Acid.—One and eight-tenths grams of the silver salt and an equivalent of benzyl chloride dissolved in 40 cc. of ether were allowed to stand in the dark for one week. After it was apparent that no reaction had occurred, the ether was removed by warming the mixture, and 40 cc. of chloroform added. After refluxing this mixture for sixty hours, the silver chloride was removed by filtration, and the filtrate heated cautiously to expel solvent; 1.6 g. of a thick yellow oil remained and this solidified in a short time on standing When recrystallized from alcohol and water a mass of lustrous plates formed; m. p. 90°.

Anal. Calcd. for $C_{20}H_{15}O_2Cl$: Cl, 10.99. Found: Cl, 11.13.

Proof of Structure of Monochloro-*m*-diphenylbenzene

Synthesis of 3-Nitro-4-chlorotoluene.—This derivative was prepared from 3-nitro-4-aminotoluene (Eastman grade) according to the procedure of Gattermann and Kaiser,[5] with the modification that the diazotization was carried out at 0° in the presence of sulfuric acid, and the resulting diazonium solution then added to the boiling CuCl–HCl mixture; yield, 44.6%.

Synthesis of **3-Amino-4-chlorotoluene.—The** above mentioned workers and also Goldschmidt and Hönig[6] prepared the amine by reduction of the nitro derivative with tin and hydrochloric acid. Iron powder and sulfuric acid was used in our work in order to avoid the formation of a dichlorotoluidine, which occurs when tin and hydrochloric acid are employed. The details of the reduction are the same as described later for the synthesis of 3-amino-4bromotoluene; yield 88.2%. Identification of our product was established through its acetyl derivative; melting point observed, 97°. The value given in the literature is 96°.

Synthesis of 2-Chloro-5-methylbiphenyl.—The method of Gomberg and Bachmann[7] for the synthesis of unsymmetrical biaryls was employed. From 75 g of 3-amino-4-chlorotoluene, 16.3 g. of a brownish yellow oil boiling at 294–304° (735 mm.) was obtained; yield, 15%; specific gravity 25/25", 1.139; refractive index (n^{25}_{D}), 1.5977.

Anal. Calcd. for $C_{13}H_{11}Cl$: Cl, 17.51. Found: Cl, 17.61.

Oxidation of 2-Chloro-5-methylbiphenyl.—Two grams of 2-chloro-5-methylbiphenyl was dissolved in glacial acetic acid and cooled to room temperature; 3.1 g. of powdered potassium permanganate was added in small portions with occasional stirring of the mixture. After standing for two hours, the mixture was made ammoniacal and filtered. The filtrate on acidifying with sulfuric acid yielded a white flocculent precipitate of 3-phenyl-4-chlorobenzoic acid. After separation of the precipitate, it was redissolved in ammonium hydroxide, filtered and reprecipitated with sulfuric acid; yield of purified product 0.5 g. (21.7%); melting point, 208–209'.

Anal. Calcd. for $C_{13}H_9O_2Cl$: Cl, 15.25. Found: Cl, 15.20.

A mixed melting point of this product and the acid obtained from the oxidation of monochloro-m-diphenylbenzene indicated that these substances were identical. From the above, it follows that the chlorination of m-diphenylbenzene produced 4-chloro-1,3-diphenylbenzene and the oxidation product of the latter was 3-phenyl-4-chlorobenzoic acid.

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(5) Gattermann and Kaiser, *Ber.*, 18, 2600 (1885).

(6) Goldschmidt and Hönig, *ibid.*, 19, 2442 (1886).

(7) Gomberg and Bachmann, THIS JOURNAL, 46, 2339 (1924).

Bromination of *m*-Diphenylbenzene

4-Bromo-1,3-diphenylbenzene.—Fifty grams of *m*-diphenylbenzene and several iron nails (freshly cleaned with hydrochloric acid) were placed in a short-necked 500-cc. round-bottomed flask to which was attached a dropping funnel and a reflux condenser. The flask was heated in a water-bath to melt the hydrocarbon and then 14 cc. of bromine (25% excess) was added very slowly from the dropping funnel, with vigorous agitation after each addition of several drops in order to minimize the quantity of higher brominated products formed. The time required for the complete addition of halogen was four to five hours. After the evolution of hydrogen bromide had ceased the reaction mixture was heated on a sand-bath to 200° to expel remaining traces of bromine and then allowed to cool to room temperature. Petroleum ether (30–60°) was then added to precipitate solid contaminants, and the reaction mixture filtered. The solvent was expelled from the filtrate by cautious heating and the residual oil fractionated under diminished pressure, Forty-two and four-tenths grams of a pale yellow viscous oil boiling at 208–213° (1 mm.) was obtained; theoretical yield, 67.1 g.; specific gravity 25/25", 1.355; refractive index (n^{25}_D) 1.6720, (n^{39}_D) 1.6653.

Anal. Calcd. for $C_{18}H_{13}Br$: Br, 25.88. Found: Br, 25.97.[8]

Olgiati prepared this derivative by allowing equivalent quantities of *m*-diphenylbenzene and bromine in the presence of carbon disulfide to stand at room temperature for three days and then warming under a reflux condenser until the reaction was complete.@ On solution of the reaction product (after removal of solvent and unreacted bromine) in a dilute alcohol–water mixture and spontaneous evaporation at low temperatures, he obtained a crystalline product melting at 31'. Numerous attempts to solidify our product were futile; even after standing several weeks in a refrigerator, the product remained an oil. Olgiati assumed the structure of this derivative from the fact that on oxidation a bromo-diphenylcarboxylic acid was obtained, and from the fact that the tetrabromo-m-diphenylbenzene (synthesized from the monobromo derivative) on oxidation yielded *p*-bromobenzoic acid and 3,4-dibromobenzoic acid. From the above he assumed that the position occupied by the fourth bromine atom was probably position 4 of the inner ring of m-diphenylbenzene. Proof for the latter conclusion was not completely established.

Oxidation of 4-Bromo-1,3-diphenylbenzene.—Six grams of 4-bromo-1,3-diphenylbenzene on oxidation with 30 g. of CrO_3 in glacial acetic acid yielded after several recrystallizations from alcohol and water 0.9 g. of pure bromophenylbenzoic acid (16.6%); melting point 242–243°. This agrees with the value reported by Olgiati for the acid.[10]

Proof of Structure of Monobromo-m-diphenylbenzene

Synthesis of 3-Nitro-4-bromotoluene.—The procedure described for the preparation of p-bromotoluene[11] was adopted for this preparation, except for the minor changes referred to below.

From 152 g. of 3-nitro-4-aminotoluene (Eastman grade), 170 g. of crude 3-nitro-4-bromotoluene was obtained by steam distillation. This was dissolved in ether and the ether layer washed with two separate 25-cc. portions of cold normal sodium hydroxide and then with water. After drying the ether layer with calcium chloride, and evaporating the solvent 153 g. of oily product remained; yield, 70.9%.

Synthesis of 3-Amino-4-bromotoluene.—To 153 g of 3-nitro-4-bromotoluene and

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(8) In several successive runs, traces of white solid appeared in the pure fraction on standing. In such eases, the treatment with petroleum ether was repeated and the oil again fractionated after removal of solvent.

(9) Ref. 1, pp. 3386–3387.

(10) Ref. 1 p. 3388.

(11) "Organic Syntheses," John Wiley and Sons, N. Y., 1926, Vol. V, p. 21.

150 cc. of water in a 3-liter flask with reflux condenser attached, 130 g. of powdered iron and 350 cc. of 18 *N* sulfuric acid were added alternately in small portions, shaking vigorously after each addition and with occasional cooling of the reaction mixture. After the last portions of iron and acid had been added, the mixture was refluxed on a water-bath for eight hours. It was then cooled, made basic with concd. sodium hydroxide and steam distilled. The distillate was extracted with ether, the ether layer dried with calcium chloride and solvent removed by distillation. A dark red oil weighing 118 g. remained; theoretical yield, 124 g. This product was purified by preparation of its acetyl derivative in the usual way, recrystallization of the latter from alcohol and water, and saponification with alcoholic potash; melting point of the acetyl derivative, 120–121°. Nevile and Winther[12] reported a value of 113.7–114 6° and Claus, 164°.[13]

Anal. Calcd. for $C_9H_{10}ONBr$: N, 6.14; Br, 35.07. Found: N, 6.18; Br, 35.43.

The purified amine is a pale yellow oil with a characteristic odor; b. p. 129–130° (16 mm.); sp. gr. 25/25° 1.474; refractive index (n^{25}_D) 1.5990. This oil gave no indication of crystallization even after standing for several months at ordinary temperatures.

Anal. Calcd. for C_7H_8NBr: N, 7.53; Br, 42.97, Found: N, 7.32; Br, 42.61.

Wroblewsky[14] prepared the base by reduction of 3-nitro-4-bromotoluene (liquid −20°) with tin and hydrochloric acid; m. p. of amine. 67°. Hübner and Roos[15] described the nitro compound with a melting point 31–32°, and its corresponding amino derivative melting at 75°. Claus[13] prepared the amine by saponification of its acetyl derivative and reported a melting point of 35°. His acyl derivative in turn was obtained by rearrangement of the oxime of 6-bromo-3-methyl-acetophenone in the presence of sulfuric acid and the latter compound was prepared from *p*-bromotoluene, acetyl chloride and aluminum chloride. Nevile and Winther[12] reported the melting point of the amine as 30.6–32°. Recently, Huston and Hutchinson,[16] following the procedure of Nevile and Winther, obtained an amine melting at 32–33°, and boiling at 115–118° (16 mm.).

We attempted the reduction of 3-nitro-4-bromotoluene employing tin and hydrochloric acid and obtained a product melting at 30–32°, but this substance after recrystallization gave qualitative tests for both chlorine and bromine. Moreover, this compound and benzene, by the Gomberg–Bachmann procedure, gave a chlorobromomethylbiphenyl, which was not investigated further. It is apparent that some of the earlier workers were nitrating mixtures of para and ortho bromotoluene without separating the desired nitro body from the mixture, while others presumably were unaware of a partial substitution of halogen in the ring when tin and hydrochloric acid were used in the reduction of the nitro derivative. Furthermore, analytical data to substantiate the purity of the particular compounds described by the above mentioned investigators is notably absent. Hence, it is very probable that Nevile and Winther were describing a chlorobromotoluidine, or a mixture of this and the expected bromotoluidine, the separation and purification of which was only partially possible under the conditions employed in their work.

In order to characterize further our 3-amino-4-bromotoluene, the benzoyl derivative was prepared. After recrystallization from alcohol and water it melted at 107.5–108.5°.

Anal. Calcd. for $C_{14}H_{12}ONBr$: N, 4.92; Br, 27.55. Found: N, 4.66. Br, 27.84.

Synthesis of 2-Bromo-5-methylbiphenyl.—From 45 g. of 3-amino-4-bromotoluene,

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(12) Nevile and Winther, *Ber.*, **13**, 972 (1880).

(13) Claus, *J. prakt. Chem.*, [2] **46**, 25 (1892).

(14) Wroblewsky, *Ann.*, **168**, 177 (1873).

(15) Hübner and Roos, *Ber.*, **6**, 800 (1873).

(16) Huston and Hutchinson, THIS JOURNAL, **54**, 1504 (1932).

diazotized and coupled with benzene as described for the preparation of 2-chloro-5-methylbiphenyl, 9.5 g. (16%) of an aromatic yellow oil boiling at 304–308° (740 mm.) was obtained; density 25/25", 1.358; refractive index (n_D^{25}), 1.6150.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.45.

Oxidation of 2-Bromo-5-methylbiphenyl.—From 1 g. of the derivative just described, and 1.5 g. of powdered potassium permanganate in glacial acetic acid, there was obtained, after following the method employed for the oxidation of 2-chloro-5-methylbiphenyl, 0.3 g. of 3-phenyl-4-bromobenzoic acid; yield 27%; m. p. 242–243°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 28.81.

A mixed melting point of this product and that obtained from the oxidation of 4-bromo-1,3-diphenylbenzene indicated that the two acids were identical. Therefore, the structure assumed by Olgiati for the monobromo derivative of m-diphenylbenzene is confirmed by the above results. Moreover, the salts and the methyl and ethyl esters derived from the bromo-diphenylcarboxylic acid described by Olgiati, are those of 3-phenyl-4-bromobenzoic acid.

In the course of the experimental proof of structure of 4-bromo-1,3-diphenylbenzene, the synthesis of 2-bromo-5-phenylbenzoic acid was also attempted, since this was the only other bromo-diphenylcarboxylic acid theoretically possible from the oxidation of 4-bromo-1,3-diphenylbenzene. The general steps taken to accomplish this end are represented schematically as follows: *m*-toluidine ⟶ *m*-acetotoluide ⟶ 3-acetamino-6-bromotoluene ⟶ 3-amino-6-bromotoluene ⟶ 3-methyl-4-bromobiphenyl ⟶ 2-bromo-5-phenylbenzoic acid. Since the first three stages in the synthesis are described elsewhere in the literature, it will suffice to report only the preparation of 3-methyl-4-bromobiphenyl. This derivative was obtained from 6-bromo-3-aminotoluene according to the method described previously for 2-chloro-5-methylbiphenyl; b. p. 318–323° (760 mm.); refractive index (n_D^{25}), 1.6358.

Anal Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.27.

All attempts to oxidize 3-methyl-4-bromobiphenyl by the methods already described in the preceding were unsuccessful, the desired product being destroyed by the oxidation. In view of this observation, it is very probable that the oxidation of 4-bromo-1,3-diphenylbenzene proceeded simultaneously with the formation of both isomeric acids, 3-phenyl-4-bromobenzoic acid and 2-bromo-5-phenylbenzoic acid, but the latter compound was destroyed and thus only the former acid was isolated.

Summary

1. The preparation and proof of structure of 4-bromo-1,3-diphenylbenzene and 4-chloro-1,3-diphenylbenzene are reported.
2. Several new unsymmetrical biaryl derivatives have been prepared and their properties determined.
3. The structure of the bromobiphenylcarboxylic acid and its methyl and ethyl esters first prepared by Olgiati, has been established.
4. An explanation of the discordant data in the literature and also the corrected physical constants for 3-amino-4-bromotoluene and its acetyl derivative are given.
5. An improved method for the purification of acids obtained on oxidation of liquid halogenated aromatic hydrocarbons with CrO_3 and glacial acetic acid has been suggested.

AKRON, OHIO

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Studies on Pyrethrum Flowers. V. The Presence of Pyrethrolon and Methyl Pyrethrolon in the Flowers

BY C. B. GNADINGER AND C. S. CORL

In 1929 Tattersfield, Hobson and Gimingham[1] published two chemical methods for evaluating pyrethrum flowers which were modifications of methods proposed by Staudinger and Harder.[2] One of these methods depended on the saponification of the pyrethrins, which are esters, and titration of the resulting acids. The other consisted of isolating the pyrethrins as semicarbazones, with subsequent estimation of the pyrethrins from the nitrogen content of the semicarbazones, determined by the Kjeldahl method. The results obtained by the two methods were in good agreement.' In the same year Gnadinger and Corl[3] described a method based on the copper-reducing action of the ketone group present in both pyrethrins. Martin and Tattersfield[4] have shown that this method agrees excellently with their own. Hartzell and Wilcoxon[6] also have found good agreement between Tattersfield's acid method and the copper reduction method Martin and Tattersfield[4] have used the principle of the writers' method to develop a fourth method which also gives results that agree with the Gnadinger and Corl method.

Thus it has been found that the four chemical methods, depending on three different reactions, yield concordant results. Martin and Tattersfield,[4] Hartzell and Wilcoxon,[5] and the writers[6] have found that the pyrethrin content, determined chemically, is correlated with the toxicity determined by biological tests on different insects.

Ripert[7] has condemned all of the methods for evaluating pyrethrum, both chemical and physiological. He claims to have isolated the methyl ether of pyrethrolon from pyrethrum flowers and states that this compound is present to the extent of 0.1 to 0.4% and would interfere with the copper reduction method, being estimated as pyrethrins without having any toxicity to insects.

In order to make clear the significance of this statement, it should be recalled that the pyrethrins are esters of the ketone alcohol pyrethrolon with chrysanthemum monocarboxylic acid or chrysanthemum dicarboxylic acid methyl ester, and the copper reducing action of the pyrethrins is due to the presence of the ketone group in the alcoholic component (pyrethrolon) of the esters.

(1) Tattersfield, Hobson and Gimingham, J. *Agr. Sci.*, **19**, 266–296 (1929).
(2) Staudinger and Harder, Ann Acad. *Sci. Fennicae*, **A29**, 1-14 (1927).
(3) Gnadinger and Corl, THIS JOURNAL, **61**, 3054 (1929).
(4) Martin and Tattersfield, J. *Agr. Sci.*, **21**, 120 (1931).
(5) Hartzell and Wilcoxon, Contribution from *Boyce* Thompson Institute, 4, 107-117 (1932).
(6) Gnadinger and Corl, THIS JOURNAL, **52**, 3300 (1930).
(7) Ripert, Ann. *fals.*, **24**, 325–341 (1931).

Ripert does not give the details of the method he employed for isolating the methyl ether of pyrethrolon from the flowers and the proof of its identity which he presents is not conclusive. His statement that the compound would interfere in the copper reduction method is not supported by any evidence.

When the copper reduction method was developed, the writers realized that pyrethrolon might be present in the flowers; the possible presence of the methyl ether of pyrethrolon was not considered. At that time pyrethrolon was prepared and its properties were investigated.

Neither pyrethrolon nor its methyl ether was found in the flowers by Staudinger and Ruzicka;[8] the thoroughness of their work makes it improbable that quantities of the methyl ether as great as Ripert reports would be overlooked. Nevertheless, it was considered advisable to investigate Ripert's claims. The results of this investigation are herewith presented.

Experimental Part

Staudinger and Ruzicka[9] called attention to the fact that the pyrethrins in petroleum ether solution are not appreciably attacked by potassium permanganate solution. They also found that pyrethrolon[10] in aqueous suspension, and pyrethrolon methyl ether[11] are immediately oxidized by potassium permanganate solution. Staudinger and Ruzicka did not investigate these reactions quantitatively nor under exactly the same conditions. The writers[12] had found that the pyrethrins in petroleum ether are scarcely attacked by potassium permanganate, while pyrethrolon under these conditions was completely oxidized and removed from the petroleum ether solution.[13] Hence this procedure might afford a means for separating the pyrethrins from pyrethrolon and possibly from pyrethrolon methyl ether.

Effect of Potassium Permanganate Solution on Pyrethrins I and 11.—The semicarbazones of pyrethrins I and II were separated from 15 kg. of Japanese ***Pyrethrum cinerariaefolium*** by a slight modification of Staudinger and Ruzicka's[8] method. The mixed semicarbazones melted at 75 to 90° and were converted into mixed pyrethrins I and II with oxalic acid solution.[8] The crude pyrethrins were purified by the writers' method[14] and were immediately dissolved in sufficient petroleum ether to make the pyrethrin content about 3.5 g. in 1000 cc. This stock solution was kept in the dark. Analysis by Tattersfield's acid method showed that the mixed pyrethrins consisted of 51.3% pyrethrin I and 48.7% pyrethrin II.

The extent to which the pyrethrins in petroleum ether are oxidized by permanganate was determined in the following manner.

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(8) Staudinger and Ruzicka. *Helv. Chim. Acta*, 7, 177–259, 377–458 (1924).
(9) Ref. 8, p. 189.
(10) Ref. 8, p. 228.
(11) Ref. 8, p. 222.
(12) Ref. 3, p. 3056.
(13) Ref. 3, p. 3060.
(14) Ref. 6, p. 3303.

An aliquot of the stock petroleum ether solution of pyrethrins was measured into a separatory funnel and diluted with sufficient petroleum ether to make the volume 100 cc.; **25** cc. of **2%** potassium permanganate solution was added and the funnel was vigorously shaken for one minute. Immediately **20** cc. of **5%** sodium bisulfite solution and **5** cc. of 15% sulfuric acid were added and the funnel was gently shaken until the excess of permanganate was destroyed. In some cases **50** cc. of 2% permanganate solution was used; in every case an excess of permanganate solution was present.

The petroleum ether and aqueous layers were separated; the former was mashed with **25** cc. of water and the aqueous layer was extracted with an equal volume of petroleum ether. This second petroleum ether extract was washed with the **25** cc. of water used to wash the original petroleum ether solution. The combined petroleum ether extracts were filtered into a 400-cc. beaker. **A** second aliquot of the stock solution of pyrethrins, equal to the first, was measured into another 400-cc. beaker and was diluted with petroleum ether to the same volume as the solution which had been treated with permanganate. The two petroleum ether solutions were then evaporated on a steam-bath and the pyrethrin content of the residues was determined by the writers' method. The results of these experiments are given in Tabie I.

TABLE I

EFFECT OF WASHING PYRETHRINS IN PETROLEUM ETHER WITH 2% PERMANGANATE SOLUTION

Aliquot taken, cc.	Pyrethrins found Not treated. mg.	Treated with $KMnO_4$, mg.	Pyrethrins lost by $KMnO_4$ treatment mg.	%
50	185.4	174.1	11.3	6.1
40	141.9	137.2	4.7	3.3
35[a]	135.6	128.6	7.0	5.2
30	106.3	100.7	5.6	5.3
25"	85.9	84.0	1.9	2.2
20	70.2	66.8	3.4	4.8
10	34.6	33.6	1.0	2.9
			Av.	4.3

[a] **50** cc. of $KMnO_4$ solution used.

The aliquots taken were selected to correspond to the pyrethrin content which would be present in pyrethrum flowers when using **15** g. of flowers for assay. The loss of pyrethrins by the permanganate treatment varied from **2.2** to 6.1%, with an average of 4.3%.

Effect of Permanganate Solution on **Pyrethrolon.—Part** of the mixed semicarbazones of pyrethrins I and II was saponified at 0° as recommended by Staudinger and Ruzicka.[15] The resulting pyrethrolon semicarbazone **was** converted into pyrethrolon by prolonged shaking with benzene and sodium bisulfate solution.[16] This pyrethrolon **(0.898** g.) was completely dissolved in petroleum ether, in which it was but slightly soluble. The petroleum ether solution was washed with 3% permanganate solution, which was instantly reduced. The washings with permanganate were continued until an excess of permanganate remained. The petroleum ether solution was then filtered and distilled in vacuum at 45° to constant weight; the residue weighed **0.012** g., that is, 98.7% of the pyrethrolon was oxidized and removed from the petroleum ether solution, by the permanganate treatment.

Effect of Permanganate Solution on **Pyrethrolon** Methyl Ether.—A second portion of the mixed semicarbazones of pyrethrins I and II was saponified at **0°** and the pyre-

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(15) **Ref.** *8*, **p. 196.**

(16) **Ref. 8, p. 216.**

throlon semicarbazone so obtained (m. p. 200–203") was used to synthesize pyrethrolon methyl ether, employing the procedure of Staudinger and Ruzicka.[17] Thirteen grams of pyrethrolon semicarbazone yielded 4.7 g. of pyrethrolon methyl ether. A small portion of the pyrethrolon methyl ether was treated with semicarbazide hydrochloride; the semicarbazone of pyrethrolon methyl ether so obtained melted at 187". This melting point is slightly higher than recorded by Staudinger and Ruzicka (183°), probably because of the presence of a small amount of pyrethrolon.

The remainder of the pyrethrolon methyl ether was dissolved in petroleum ether, the concentration being 0.643 g. per 100 cc. Aliquots of this solution were treated with permanganate solution exactly as described above in the case of the pure pyrethrins, and the copper reducing power of the permanganate treated solution was compared with that of a solution of the same pyrethrolon methyl ether content which had not been treated with permanganate. Since no tables have been calculated for the copper reducing power of pyrethrolon methyl ether, it was necessary to express its reducing power, in Table II, in terms of the amount of dextrose having equivalent copper reducing power.

TABLE II

EFFECT OF TREATING PYRETHROLON METHYL ETHER IN PETROLEUM ETHER WITH 2% PERMANGANATE SOLUTION

Pyrethrolon methyl ether, mg.	Permanganate soln. used, cc.	Dextrose equivalent in reducing power to pyrethrolon methyl ether		Pyrethrolon methyl ether lost by $KMnO_4$ treatment, %
		Not treated with $KMnO_4$, mg.	Treated with $KMnO_4$, mg.	
128.6	25	13.84	6.25	54
128.6	50	13.84	0.00	100
64.3	25	6.41	0.00	100

In the first experiment (Table II) the permanganate solution was completely reduced by about half the pyrethrolon methyl ether taken. When the amount of permanganate was doubled, or the quantity of pyrethrolon methyl ether was halved, the copper reducing power of the pyrethrolon methyl ether was completely destroyed. The amounts of pyrethrolon methyl ether taken were several times greater than would be encountered in assaying pyrethrum flowers containing the amount of pyrethrolon methyl ether Ripert claims to have found. It should also be noted that the copper reducing power of pyrethrolon methyl ether is somewhat less than that of the pyrethrins. This was also true of pyrethrolon.[18]

Effect of Permanganate on Petroleum Ether Extract of Pyrethrum Flowers.—From the foregoing experiments it is quite clear that the pyrethrins can be separated, with slight loss, from pyrethrolon or pyrethrolon methyl ether by treating them, in petroleum ether, with 2% potassium permanganate solution.

According to Ripert,[19] methyl pyrethrolon is the form in which the reserve of pyrethrolon is stored by the plant, pending esterification with the chrysanthemum acids by metabolic processes. If this is the case one would expect to find larger quantities of methyl pyrethrolon in freshly harvested flowers than in flowers several months old. In Table III are given the analyses of samples of pyrethrum flowers assayed as soon as possible after harvesting. Two series of 15-g. samples of the ground flowers were extracted with petroleum ether in Soxhlet extractors. One series of petroleum ether extracts was assayed by the writers' method. Another series of petroleum ether extracts was first treated with 2% permanganate solution exactly in the manner described above, before assaying.

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(17) Ref. 8, p. 222.

(18) Ref. 3, p. 3060.

(19) Ref. 7, p. 340.

TABLE III

EFFECT OF PERMANGANATE TREATMENT ON PYRETHRIN CONTENT OF FRESHLY HARVESTED PYRETHRUM FLOWERS

Where grown	Harvested	Assayed	Pyrethrin content of flowers: Not treated with $KMnO_4$, %	Treated[a] with $KMnO_4$, %	Loss of pyrethrins by $KMnO_4$ treatment: %	% of pyrethrin content
Colorado	7/14/32	7/21/32	1.04	1.00	0.04	3.8
Wakayama. Japan	6/15/32	8/9/32	1.00	0.94	.06	6.0
Spalato, Dalmatia	5/27/32	7/19/32	0.84	.79	.05	5.9
				Av.	.05	5.2

[a] 50 cc. of 2% $KMnO_4$ used.

The average loss in pyrethrin content of the flowers by the permanganate treatment is 0.05% equivalent to 5.2% of the total pyrethrins present. This is only 0.9% greater than the loss with pure pyrethrins (4.3%, see Table I). This indicates that pyrethrolon and pyrethrolon methyl ether are not present in flowers shortly after harvesting.

Ten additional samples of pyrethrum flowers from different sources were assayed ten months after they were harvested. These samples were assayed by the copper reduction method both with and without the permanganate treatment. The results are compared in Table IV.

TABLE IV

EFFECT OF PERMANGANATE TREATMENT ON PYRETHRIN CONTENT OF PYRETHRUM FLOWERS TEN MONTHS OLD

Where grown	Grade	Pyrethrin content of flowers: Not treated with $KMnO_4$, %	Treated with $KMnO_4$, %	Loss of pyrethrins due to $KMnO_4$ treatment: %	% of pyrethrin content
Rose, Dalmatia	Half closed	0.70	0.59	0.11	15.7
Trogir. Dalmatia	Mixed	.76	.65	.11	14.4
Trogir, Dalmatia	Closed	.71	.59	.12	16.9
Hokkaido, Japan		.76	.68	.08	10.5
Hokkaido. Japan	......	.79	.69	.10	12.6
Hokkaido. Japan	......	.71	.59	.12	16.9
Hokkaido, Japan		.85	.72	.13	15.3
Hokkaido, Japan		.86	.72	.14	16.3
Hokkaido, Japan	......	1.01	.85	.16	15.8
Cyprus	Closed	0.75	.63	.12	16.0
			Av.	.12	15.0

The loss in pyrethrin content averaged 0.12% of the weight of the flowers, equivalent to 15.0% of the pyrethrins present. The losses are fairly constant for flowers from different countries and of different pyrethrin contents. Correcting for the loss due to the effect of permanganate on pure pyrethrins (4.3%), the average loss in these ten-month old flowers, due to other oxidizable material, is 10.7% of the pyrethrins present. In the freshly harvested flowers the corrected loss was 0.9%.

The writers[20] have shown that the pyrethrin content of pyrethrum flowers becomes gradually reduced as the flowers age, the loss amounting to about 30% in one year. This loss of pyrethrins is due to oxidation or to a molecular rearrangement and is accelerated by light.[5,21] The altered pyrethrins are almost insoluble in petroleum ether, the

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(20) Gnadinger and Corl, *Ind. Eng. Chem.*, **24**, 901 (1932).

(21) Tattersfield, *J. Agr. Sci.*, 396–417 (1932).

solubility being 3.6 mg. per 100 cc. at 20°. Their copper reducing power is slightly higher than that of the pyrethrins. Whether they are oxidized in petroleum ether solution by permanganate was not determined because of their low solubility in that solvent.

In ether, however, a considerable oxidation of altered pyrethrins occurs when the permanganate treatment is applied. An ether solution containing 88 mg. of pyrethrins altered by exposure to air at room temperature was washed with 25 cc. of saturated permanganate solution. The ether solution was evaporated and the residue was weighed; 62 mg. of altered pyrethrins was lost by oxidation. A second ether solution containing 176 mg. of altered pyrethrins was treated with permanganate in the same manner as the pure pyrethrins, as previously described. The loss by the permanganate treatment was 45 mg. The altered pyrethrins are apparently more readily attacked than pyrethrins I and II and it is quite probable that the altered pyrethrins in the samples reported in Table IV were oxidized by the permanganate treatment. This would account, in part, for the fact that old flowers show a greater loss in pyrethrin content when treated with permanganate than new flowers similarly treated.

Summary

1. A method is described for separating pyrethrolon and its methyl ether from pyrethrins I and II.

2. The pyrethrins in petroleum ether are not readily oxidized by dilute permanganate solution, the loss averaging about four per cent.

3. Pyrethrolon and pyrethrolon methyl ether, in petroleum ether, are instantly oxidized by dilute permanganate solution and removed from the petroleum ether.

4. Pyrethrins altered by exposure to air are, in ether solution, appreciably oxidized by permanganate solution.

5. Freshly harvested pyrethrum flowers assayed by the permanganate method show about the same loss of pyrethrins as solutions of pure pyrethrins of the same strength.

6. Pyrethrum flowers ten months old show a somewhat greater loss by the permanganate method, probably because of the oxidation of altered pyrethrins.

7. No evidence of any appreciable amount of pyrethrolon or pyrethrolon methyl ether was found in flowers from America, Dalmatia or Japan.

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Hydroxyphenyl Alkyl Sulfides[1]

BY ELLIS MILLER AND R. R. READ

In their study of the antiseptic properties of phenolic sulfur combinations, Hilbert and Johnson[2] discovered that p-hydroxydiphenyl sulfide possessed greater germicidal power than was then shown by the most active members of the alkylated phenol family. Since this unusual activity appeared to be due largely to the sulfur linkage, it was felt by the authors that even more striking results might be obtained by substituting an alkyl group for one of the phenyl groups in this compound. Accordingly, they undertook the synthesis of a series of hydroxy-phenyl alkyl sulfides of which a number are described in this paper.

Experimental

The procedure first used was an adaptation of the method of Hilbert and Johnson. It was found that diazotized phenetidine would couple with mercaptans as readily as with thiophenol. However, in order to simplify the process and, especially, to eliminate the dealkylation step, use was made of the Leuckart[3] reaction, which depends upon the greater reactivity of the sulfhydryl group in thiohydroquinone as compared with the hydroxyl group. Thiohydroquinone is prepared by coupling diazotized *p*-aminophenol with ethyl potassium xanthate. Leuckart prepared p-hydroxyphenyl ethyl sulfide by converting thiohydroquinone into the lead salt through lead acetate and heating it in alcoholic suspension with ethyl iodide. The authors found, in preparing the other members of the series, that the mono-sodium salt of thiohydroquinone in methyl alcohol solution was even more effective than the lead salt.

Since the methods of preparation are uniformly applicable to any member of the series, only one example, that of p-hydroxyphenyl butyl sulfide, will be given. The other members thus prepared, together with their physical constants and analyses, are shown in the accompanying table.

Preparation of **Thiohydroquinone.**—110 grams of p-aminophenol (1.0 mole) was dissolved in an excess of 10% hydrochloric acid (2.25 moles). The solution was cooled below 15° and was diazotized by the gradual addition of 70 g. of sodium nitrite (1.0 mole), the temperature being maintained at 15 to 20° by means of ice.

The diazo solution was then run slowly beneath the surface of a hot solution of 224 g. of potassium ethyl xanthate (1.4 moles) in 650 g. of water, the reaction mixture being stirred vigorously and kept at 70 to 75° to ensure complete decomposition of the intermediate diazo combination. When all the diazo was in, the temperature was raised to 90° and maintained for a half hour. The xanthate ester was then decomposed by adding 160 g. of solid sodium hydroxide (4 moles) and refluxing for several hours, the mixture being then strongly acidified with an excess of 50% sulfuric acid and further refluxed in the presence of zinc and benzene in order to reduce any disulfide which may have been formed. The crude thiohydroquinone was separated as an oil, washed with dilute hydrochloric acid and water, and distilled in *vacuo*. There was obtained 61 g. of a clear colorless liquid, boiling at 133–137° (11 mm.).

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(1) Cf. Miller and Read, THIS JOURNAL, **54**, 4113 (1932).

(2) Hilbert and Johnson, *ibid.*, 61, 1526 (1929).

(3) Leuckart, *J. prakt. Chem.*, [2] 41, 193 (1890).

TABLE I

STRUCTURAL, PHYSICAL AND ANALYTICAL DATA

A number of chain-substituted derivatives of hydroxyphenyl alkyl sulfides have been prepared and will be described later.

Side chain on phenol	Position	Phenol coefficient[a]	M. p., °C.	B. p., °C.	Analyses, % *S* Calcd.	Analyses, % *S* Found
$—SCH_3$	*p*	8	...	113 (6 mm.)		
$—SCH_2CH_3$[b]	p	10	41	153–155 (13 mm.)	...	...
$—SCH_2CH_2CH_3$	*p*	36	37	150–153 (5–6 mm.)	19.6	18.93
$—SCH_2CH_2CH_2CH_3$	*p*	77	49–50	166–168 (7 mm.)	17.6	17.4
$—SCH_2CH_2CH_2CH_2CH_3$[c]	*p*	120	59	175–180 (8–10 mm.) 164–168 (3–4 mm.)	16.35	16.79
$—SCH_2CH_2CH_2CH_2CH_2CH_3$	*p*	0[d] 230[e]	60	194–196 (16 mm.) 178–180 (5 mm.)	15.2	15.64
$—SCH_2C_6H_5$	*p*	0[d] <20[e]	104	220–225 (15 mm.)	14.8	14.79
$—SCH(CH_3)_2$	*p*	20	...	150–152 (13 mm.)	19.1	19.38
$—SCH_2CH(CH_3)_2$	*p*	61	...	159–162 (10 mm.)	17.6	17.79
$—SCH_2CH_2CH(CH_3)_2$	*p*	30	...	150–152 (3 mm.)	16.35	16.44
$—SCH_2CH_2CH_2CH_3$	*o*	25	...	110–112 (5 mm.)	17.6	17.91
$—SCH_2CH_2CH_2CH_3$	*m*	40	...	127–140 (4 mm.)	17.6	17.1

[a] Phenol coefficients by the hygienic Laboratory method, 20°, *Staph. aureus.*

[b] This product was reported by Leuckart, Ref. 3. No analysis was made, since its melting point checked that given in the literature.

[c] This product was recently reported by Moness, Braker and Christiansen [*J. Am. Pharm. Assoc.*, 21, 565 (1932)], who describe it as an oil boiling at 123–130° (2–3 mm.).

[d] The coefficient measured by the usual procedure was 0, *i. e.*, a saturated solution was inert.

[e] When these products were dissolved 1:1000 in *N*/100 sodium hydroxide and further dilutions made with water, the values 230 and 20 were obtained. The solubility of the n-hexyl sulfide is apparently less than 1:10,000 in water.

I. ***p*-Hydroxyphenyl** Butyl Sulfide by the Thiohydroquinone Method.—Twenty grams of sodium hydroxide (0.5 mole) was partially dissolved in 50 g. of methyl alcohol and to this added a solution of 58.3 g. of thiohydroquinone (0.55 mole) in 50 g. of methyl alcohol. The mixture was stirred while 68 g. of n-butyl bromide (0.5 mole) was being added during the course of fifteen minutes. Reaction set in at once and proceeded vigorously with evolution of heat and formation of a voluminous precipitate of sodium bromide. The mass was refluxed for about an hour, allowed to cool and filtered. The filtrate was distilled to remove methyl alcohol, the residual oil washed with water, extracted with benzene and distilled *in vacuo.* A major fraction of p-hydroxyphenyl butyl sulfide was obtained, boiling at 165–8° (7 mm.). It solidified on standing to a white crystalline mass which was recrystallized from ligroin and melted at 49–50°. The yield was practically theoretical.

II. ***p*-Hydroxyphenyl** Butyl Sulfide by the **Mercaptan Method.**—68.5 grams of *p*-phenetidine (0.5 mole) was dissolved in an excess of 10% hydrochloric acid (1.25 moles); the solution was cooled below 15° and diazotized by the gradual addition of 35 g. of sodium nitrite (0.5 mole), the temperature being maintained at 15–20° by means of ice.

The diazo solution was then run slowly beneath the surface of a hot solution of 49.5 g. of n-butyl mercaptan (0.55 mole) in 400 g. of 20% caustic soda, care being taken to stir the mixture vigorously and to maintain the temperature at 70–75°. When all the diazo was in, the temperature was raised to 90° and maintained until no further evolution of nitrogen could be observed. The solution was then allowed to cool down to room temperature and acidified with concentrated hydrochloric acid. A heavy black oil separated. The oil was washed with dilute hydrochloric acid and with water and then distilled *in vacuo*, yielding an intermediate product—*p*-ethoxyphenyl butyl sulfide (b. p. 150–60° (12 mm.)). This ether was de-ethylated by refluxing at 75–85° for six hours with an excess (3 moles) of 20% hydrobromic acid in glacial acetic acid and the excess hydrobromic: acetic acid mixture was removed by vacuum distillation. Ester present in the residual oil was hydrolyzed by refluxing with 10% caustic soda dissolved in 25% alcohol and the alcohol distilled off, leaving in solution the sodium salt of *p*-hydroxyphenyl butyl sulfide. This solution was extracted a number of times with benzene to remove any unchanged ether and the aqueous solution acidified with hydrochloric acid. The oil which separated was taken up with benzene, washed with water and distilled in *vacuo*. A white crystalline product resulted similar in all respects to the *p*-hydroxyphenyl butyl sulfide obtained by the first method.

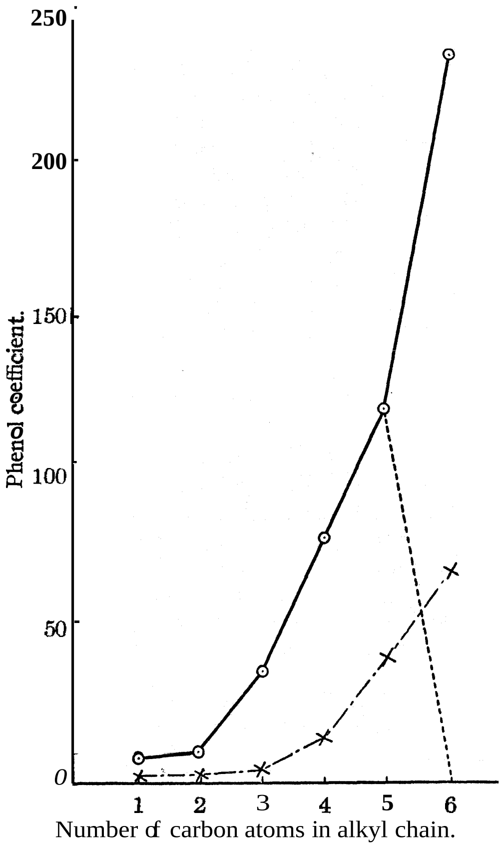

Fig. 1.—Curve ——, bactericidal activity of an homologous series of *p*-hydroxyphenyl *n*-alkyl sulfides. In the case of the hexyl derivative, it is necessary to use $N/100$ alkali, instead of water, to bring it into solution; otherwise no activity is observed, as is indicated by the broken line of the curve. Curve — . — · —, bactericidal activity of a corresponding series of *p*-hydroxyphenyl *n*-alkyl oxides. The oxygen linkage is thus seen to be far less effective than sulfur in augmenting germicidal activity.

In the foregoing examples, the *n*-butyl bromide of Example I may be replaced by any other alkyl halide and the *n*-butyl mercaptan of Example II may be replaced by any other alkyl mercaptan to give the corresponding *p*-hydroxyphenyl alkyl sulfide. Aralkyl halides and mercaptans may also be used to produce the corresponding products.

Preliminary values for the germicidal activity of this series indicates that, except for a higher level of activity, the same relation holds for thioalkyl phenols as for alkyl phenols, namely, that the phenol coefficient increases with increase in the length of the side chain; and that the normal chain compound is more active than the corresponding branched chain derivatives. They differ, however, in the effect of position isomerism, as shown by the three isomeric hydroxyphenyl butyl sulfides. In marked contrast, the three isomeric butylphenols[4] show no variation whatever.

This phase of the subject will be dealt with more fully in a later paper.

Summary

1. A series of hydroxyphenyl alkyl sulfides has been prepared.
2. A preliminary bactericidal study of these compounds has been made, which indicates that they are more powerful than corresponding alkyl phenols.
3. The investigation of phenol alkyl sulfides is being continued in this Laboratory.

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(4) Read and Miller, THIS JOURNAL, 54, 1106 (1932).

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Capric Acid from the Seed Fat of the California Bay Tree

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In 1882 Stillman and O'Neill[1a] reported the isolation of an eleven carbon acid, which they called "umbellulic acid," from the seed fat of the California laurel or bay tree (*Umbellularia californica*). Lewkowitsch[2] states that "umbellulic acid" is really lauric acid, but the only other reference to work on this fat that we have been able to find is a further note by Stillman and O'Neill[1b] stating that their previous work was in error and that they were dealing with a mixture of fatty acids, one of which was lauric acid.

Because their original analyses indicated an eleven carbon acid, it seemed likely to us that they were dealing with a mixture of capric and lauric acids. Accordingly a quantity of the seeds was collected, shelled and ground through a food chopper, and the fat extracted with hot carbon tetrachloride. On evaporating the solvent, the fat to the extent of 58.5% of the ground nuts was obtained, a yield almost identical with the 59% previously reported.'' The physical and chemical constants of the fat were as follows: m. p. 28–30°; saponification number, 275.1; unsaponifiable material, 2.1%; iodine number, 5.7; acid number, 2.8. The fat showed no optical rotation in chloroform solution.

The methyl esters of the fatty acids were prepared by alcoholysis of 530 g. of fat and separated by four fractional distillations at a pressure of 17.5 mm. using a lagged 30-cm. column of the Vigreux type. There were obtained two main fractions boiling at 119–122° and 145–147°, which weighed 133 g. (28%) and 256 g. (54%), respectively. Saponification equivalents of 187 and 213 indicated that they consisted of pure methyl caprate and pure methyl laurate. The remainder of the material, 84 g. (18%), was almost uniformly distributed among eight other fractions distilling from below 115" to above 153°.

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(1) (a) Stillman and O'Neill, *Am.* Chem. J., 4,206 (1882): (b) ibid., 98,817 (1902).

(2) Lewkowitsch, "Oils, Fats and Waxes," 6th ed., 1921, Vol. I, p. 158.

In order to get a better estimation of the relative amounts of the acids present in the fat, the saponification equivalents of all the fractions were determined. Assuming the intermediate fractions to be composed solely of the pure higher and lower boiling main fractions, the mixed esters were found to consist of **0.9%** methyl caprylate, **37.5%** methyl caprate[3] and 61.6% methyl laurate. Fractionation of a 1630-g. lot of fat gave almost identically the same results.

Although the iodine value would indicate the presence of about 6% of oleic acid, the saponification equivalents of the highest fractions of the methyl esters gave no indication of any acids of higher molecular weight than lauric. The presence of caprylic acid and absence of lower acids were shown by fractionating at atmospheric pressure all the fractions below methyl caprate from the total 2160 g. of fat. A pure methyl caprate fraction was isolated but no lower boiling ester.

The three acids were positively identified by saponifying the esters and converting the free fatty acids into the amides. These showed no depression in melting point when mixed with the amides prepared from specimens of caprylic, capric and lauric acids obtained from coconut oil.

Summary

The chemical constants of the seed fat of the California bay tree have been determined and the composition of the free fatty acids studied by fractionating their methyl esters. This showed that the fat is an excellent source of capric acid since the free fatty acids consist of approximately 1% caprylic, **37%** capric and 62% lauric acids.

(3) This is by far the best source of capric acid. For other sources see Taylor and Clarke, THIS JOURNAL, 49, 2829 (1927); Marvel and Hager, *ibid.*, 46, 726 (1924); Kao and Ma, J. *Chem. Soc*, 2047 (1931)

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CALIFORNIA

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[CONTRIBUTION FROM THE SYNTHETIC ORGANIC CHEMISTRY DEPARTMENT OF THE EASTMAN KODAK COMPANY]

The Preparation of Furil

BY W. W. HARTMAN AND J. B. DICKEY

In recent years furil dioxime has found favor as an analytical reagent. A new method for the preparation of furil from inexpensive materials should prove to be of interest.

Furil can be prepared by the oxidation of furoin in alkaline alcoholic solution with oxygen,[1] iodine[2] and nitrobenzene.[3] The method described in the Experimental Part is an application of a method for the preparation of benzil.[4]

Experimental

Furoin.—The furoin used was prepared in slightly improved yields[5] by a modification of the method of Fischer.[6] In a 22-liter flask fitted with a mechanical stirrer, an

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(1) Fischer, Ber., 13, 1337 (1880); *Ann.*, 211, 218 (1882).

(2) Corson and McAllister, THIS JOURNAL, 51, 2822 (1929).

(3) Nisbet, *J. Chem. Soc.*, 3121 (1928).

(4) Clarke and Dreger, Org. *Syn. Coll.*, 1, 80 (1932); Fischer, Ann., 211, 214 (1932).

(5) The best yield reported previous to this is 25%

(6) Fischer, Ann., 211, 218 (1882).

S-tube with dropping funnel, and an inverted Liebig condenser, were placed 8 liters of water, 4 kg. (41.65 moles) of freshly distilled furfural,[7] and 3 liters of 95% of ethyl alcohol. The reaction mixture was then heated to boiling and the flame was removed. When the liquid had just ceased to boil, a solution containing 200 g. (3.07 moles) of potassium cyanide dissolved in 600 cc. of water was added with stirring as rapidly as the vigor of the reaction would permit. The reaction mixture boiled for twenty minutes (heat of reaction) and was then heated to boiling for an additional five minutes. The alkaline solution was made acid to litmus with glacial acetic acid and placed in a cool place to crystallize overnight. The resulting mass of dark-colored tarry crystals was filtered on a large Buchner funnel and washed with cold water followed by cold methyl alcohol to remove as much of the tar as possible. Then the brown-colored residue was crystallized from methyl alcohol using 200 g. of "Norit" decolorizing carbon. The furil separated as light-brown needles melting at 134–135°. The yield of purified material is 1500 *g.*, which is 37.5%.

Furil.—In a 1-liter round-bottomed flask fitted with a mechanical stirrer was placed 158 g. (0.63 mole) of powdered copper sulfate ($CuSO_4 \cdot 5H_2O$), 210 g. of pyridine (b. p. 109–118°) and 90 g. of water. The stirrer was started and the mixture was heated on a water-bath until solution was effected. To the solution was added 57.6 g. (0.3 mole) of furoin (m. p. 134–135°). After a short time the color of the reaction mixture changed from a deep blue color to a deep green with a brownish tinge. Stirring and heating were continued for two hours and the reaction mixture[8] was poured into 1 liter of cold water, filtered on a Büchner funnel, and washed with water until the wash water was colorless. The black residue was then washed with 500 cc. of cold methyl alcohol and recrystallized from methyl alcohol,[9] using 25 g. of "Norit" decolorizing carbon. Yellow needles were obtained melting at 165–166°. The yield of purified material was 35.9 g., or 63%. A yield of 64% was obtained from a run ten times that described above.

Summary

An improved method for the preparation of furoin has been described. Furoin can be oxidized to furil by means of copper sulfate in excellent yields.

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(7) The furfural was distilled from a water bath under reduced pressure (20–30 mm.).

(8) If desired, the reaction mixture can be cooled and the furil removed by filtration. The solution is reactivated by passing oxygen into it.

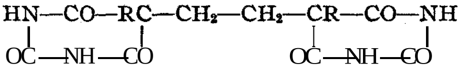
(9) Furil can be crystallized satisfactorily from benzene.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY. PAPER NO. 469]

Ethylene-N,N'-bisbarbital, a Dimolecular Barbital with Hypnotic Properties

BY ARTHUR W. DOX

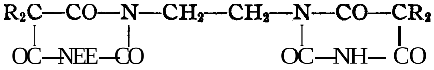
Structures previously synthesized containing two dialkylbarbituric acid groupings in the molecule are represented by the type



$$\begin{array}{lllllllll} \mathrm{HN} & - \mathrm{CO} - & \mathrm{RC} & - \mathrm{CH_2} - \mathrm{CH_2} - & \mathrm{CR} & - \mathrm{CO} - & \mathrm{NH} \\ | & & | & & | & & | \\ \mathrm{OC} & - \mathrm{NH} - & \mathrm{CO} & & \mathrm{OC} & - \mathrm{NH} - & \mathrm{CO} \end{array}$$

where the two heterocycles are joined at the 5-C through an ethylene chain. Derivatives of this type, with R = ethyl, propyl and benzyl, were prepared in 1911[1] by condensation of ethyl 1,4-dialkylbutane-1,1,4,4-tetracarboxylate with urea. The substances are described as having no melting point up to 300°, and no mention is made of their physiological properties. From the fact that no synthetic hypnotics are known with melting points above 200°, it may be assumed that these products were physiologically inert.

Another type of dimolecular barbital is possible, in which the two barbituric acid groupings are joined at the 1-N through an ethylene chain. This type is represented by the formula



$$\begin{array}{lllllllll} \mathrm{R_2C} & - \mathrm{CO} - & \mathrm{N} & - \mathrm{CH_2} - \mathrm{CH_2} - & \mathrm{N} & - \mathrm{CO} - & \mathrm{CR_2} \\ | & & | & & | & & | \\ \mathrm{OC} & - \mathrm{NEE} - & \mathrm{CO} & & \mathrm{OC} & - \mathrm{NH} - & \mathrm{CO} \end{array}$$

and should result from condensation of ethyl diethylmalonate with ethylenediurea. More strictly considered, this type might also be regarded as a trialkylbarbituric acid derivative[2] in which the N-alkyl of each of two molecules is linked together.

Experimental

Ethylenediurea was prepared in 1861 by Volhard[3] from ethylenediamine hydrochloride and silver cyanate, but has not appeared in subsequent literature. The product used in this work was obtained in 70% yield from the diamine hydrochloride and potassium cyanate instead of the more costly silver cyanate, and readily purified by crystallization from hot water.

Ethylene-N,N'-bisbarbital.—Condensation of ethylenediurea with two moles of ethyl diethylmalonate was effected by heating the mixture with a 10% alcoholic solution of sodium ethoxide for seven hours at 100–106°, according to the usual procedure for barbituric acid synthesis. The sodium salt of the product, which separated out on cooling, was filtered and washed with alcohol. It dissolved readily in water and gave a crystalline separation of the free acid when the solution was acidified with hydrochloric acid. By recrystallization from alcohol the acid was obtained in slender needles, melting at 189'. A mixed melting point with barbital (m p. 191°) showed a depression of about 30°. The yield was 75%.

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[1] German Patent 233,968 (1911).

[2] Dox and Hjort, *J. Pharm. Exp. Therapeutics*, *81*, 455 (1927).

[3] Volhard, *Ann.*, **119**, 349 (1861).

Anal. Calcd. for $C_{18}H_{26}O_6N_4$: C, 54.82; H, 6.60; N, 14.21. Found: C, 54.06; H, 6.50; N, 14.22.

Ethylene-N,N'-bis(5-hexyl-5-ethylbarbituric acid).—The same procedure was followed, using ethyl hexylethylmalonate[4] in place of ethyl diethylmalonate. The sodium salt of the product was soluble in alcohol and did not separate on cooling the reaction mixture, as did the lower homolog. The alcohol was removed by evaporation, the pasty residue taken up in water and the free acid precipitated by addition of hydrochloric acid. The free acid was a colorless transparent gum which solidified to a vitreous mass and softened again on warming. It was readily soluble in most organic solvents, including petroleum ether, but has not thus far been induced to crystallize. Since the molecule contains two asymmetric C-atoms, the failure of the product to crystallize may be attributed to the presence of two pairs of optical isomers.

Anal. Calcd. for $C_{26}H_{42}O_6N_4$: C, 61.66; H, 8.30, N, 11.07. Found: C, 60.40; H, 8.43; N, 11.19.

Ethylenebis(carbethoxyurea), $C_2H_5O_2CNHCONHCH_2CH_2NHCONHCO_2C_2H_5$.—Reaction between ethylenediurea and ethyl phenylethylmalonate. This reaction was expected to yield the analogous ethylene-N,N'-bisphenobarbital. Although the condensation was repeatedly performed at various reaction temperatures, the main product was in each instance an alkali-insoluble substance with none of the properties of a barbital. Recrystallization from a large volume of alcohol, in which the substance is difficultly soluble, gave colorless needles melting at 219" with evolution of gas. The yield was 50–58%.

Anal. Calcd. for $C_{10}H_{18}O_6N_4$: C, 41.38; H, 6.21; N, 19.31. Found: C, 41.38; H, 6.31; N, 19.09.

The empirical formula does not correspond to that of any possible barbital, but coincides with that of ethylenebis(carbethoxyurea). The latter, being an allophanic ester, should react with ammonia to form the corresponding biuret, and thus establish its identity.

Ethylenebisbiuret, $H_2NOCNHCONHCH_2CH_2NHCONHCONH_2$.—The product just described was heated several hours with 25% ammonia in a sealed tube at 100°. The crystals did not dissolve perceptibly but gradually assumed a more granular appearance. The product, which was practically insoluble in water or alcohol, was washed and dried. It melted at 245° with evolution of gas.

Anal. Calcd. for $C_6H_{12}O_4N_6$: C, 31.03; H, 5.17; N, 36.21. Found: C, 30.65; H, 5.31; N, 35.12.

Further proof of the identity of the $C_{10}H_{18}O_6N_4$ compound was obtained by preparing ethylenebis(carbethoxyurea) by a method generally applicable to the preparation of allophanic esters.[5] Ethylenediurea and alcoholic sodium ethoxide were heated six hours at 95–100° with an excess of ethyl carbonate. The reaction mixture was evaporated to dryness, the residue washed with water and recrystallized from a large volume of alcohol. The yield was 77.4% of needle-shaped crystals which melted at 219° with evolution of gas, and gave no melting point depression when mixed with the $C_{10}H_{18}O_6N_4$ product.

The so-called "biuret reaction" for proteins and their high molecular products of hydrolysis was applied to both the allophanic ester and the biuret derivative. With sodium hydroxide and a trace of copper sulfate, the former gave a deep blue and the latter a deep pink color, although both substances are nearly insoluble.

The formation of an allophanic ester in the condensation of a substituted malonic ester with a urea was quite beyond the writer's experience in the preparation of numerous

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(4) Dox, This Journal, 46, 1709 (1924).

(5) German Patent 427,417 (1926).

barbituric acid derivatives. No such reaction is mentioned in the literature. Empirically it represents an exchange of carbethoxyl for hydrogen between the two reacting substances. A second product of the reaction should then be ethyl phenylethylacetate. This was isolated by ether extraction of the mother liquor and identified as the free acid (a-phenylbutyric) after hydrolysis. The acid melted at 42°, boiled at 270–275° and showed molecular weight by titration 163; theoretical 164.

A control experiment in which ethylenediurea and sodium ethoxide were heated in the absence of ethyl phenylethylmalonate yielded no trace of the ethyl ethylenediallophanate. Two moles of ethylenediurea might conceivably split off two ammonia to form a fourteen-membered cyclic biuret which might then undergo alcoholysis into the ethylenebis(carbethoxyurea) and ethylenediamine. The possibility of such a reaction having occurred seems to be excluded by the failure to obtain any trace of the allophanate when the ethyl phenylethylmalonate was omitted.[6]

Physiological Action

Tests by intraperitoneal injection of the sodium salt of ethylenebisbarbital in white mice showed hypnotic potency equal to about three-fourths that of barbital. The homologous hexyl derivative administered in the same way was much feebler in its action. A 2-mg. dose caused very noticeable drowsiness in a 20-g. mouse but no anesthesia. An increase to two and four times this dosage gave precisely the same effect as the smaller dose. Evidently the limiting factor here is the rate of absorption which in turn is limited by the insolubility of the free acid.

Summary

Ethylene-N,N′-bisbarbital, the double structure consisting of two barbital molecules joined at the nitrogen through an ethylene chain, retains the hypnotic properties of the components. This is in contrast to a previously known structure where the connecting chain was attached to carbon instead of nitrogen.

The homologous ethylene-N,N′-bis(5-hexyl-5-ethylbarbituric acid) is much feebler in physiological action than its hexylethylbarbituric acid components.

Attempts to prepare the analogous ethylene-N,N′-bisphenobarbital by the same procedure resulted in the formation of ethylenebis(carbethoxyurea)—an allophanic ester derivative identified by analysis and by conversion into ethylenebisbiuret—and ethyl phenylethylacetate. The reaction appears to be an exchange of carbethoxyl for hydrogen instead of the usual barbituric acid condensation.

DETROIT, MICHIGAN

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(6) An excellent paper by Cope and McElvain [THIS JOURNAL, 64, 4319 (1932)] which appeared shortly after the writer's manuscript had been submitted for publication, furnishes a simple explanation for the above reaction in which an allophanic ester is obtained instead of the expected barbituric acid. As shown by Cope and McElvain, ethyl ethylphenylmalonate forms an addition product with sodium ethoxide, and this on warming decomposes into the sodium enolate of ethyl ethylphenylacetate and ethyl carbonate. The latter would then react with the urea derivative in the presence of sodium ethoxide to form the corresponding allophanic ester, just as in the above synthesis performed according to the German patent.

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

A Study of the Cyclization of a Series of ω,ω'-Dicarbethoxydialkylmethylamines through the Acetoacetic Ester Condensation

BY E. A. PRILL AND S. M. MCELVAIN

There are numerous examples in the literature of the application of an internal acetoacetic ester condensation (the Dieckmann reaction) to the synthesis of cyclic β-keto esters. Dieckmann[1] first used this reaction for the synthesis of five, six and seven membered alicyclic ring structures. In the heterocyclic field use has been made of this reaction in the preparation of both monocyclic and bicyclic systems containing nitrogen as the hetero atom.[2] In this Laboratory the reaction has been applied to the preparation of a number of 1-alkyl-3-carbethoxy-4-piperidones from β,β'-dicarbethoxydiethylalkylamines.[3]

The present paper reports an extension of this work to a series of ω,ω'-dicarbethoxydialkylmethylamines, of the type $C_2H_5OOC(CH_2)_mN(CH_3)(CH_2)_nCOOC_2H_5$, and in which both m and n are varied from 1 to 4. It was the purpose of this work to prepare derivatives of 3-pyrrolidone,[4] the heretofore unknown 3-piperidone, and as many of the larger ring analogs of these cyclic amino ketones as possible.

Sodium ethoxide was used as a condensing agent instead of metallic sodium which had been used in the earlier work.[3] Also three different conditions of reaction, *viz.*, no solvent, benzene as a solvent, and xylene as a solvent, were employed with the various di-esters. It seemed likely that intramolecular rather that intermolecular condensation would be favored by dilution with an inert solvent in those cases where ring formation is more difficult. The alcohol generated in the condensation was removed by distillation as it was formed and its amount determined by direct weighing when no solvent was used, by refractive index of the distillate when benzene was the solvent, and by the phthalic anhydride method[5] in those cases in which xylene was used. By this procedure a more complete reaction was assured and the rate, extent and type of condensation could be roughly determined.

The details of the preparation of the various ω,ω'-dicarbethoxydialkyl-

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(1) Dieckmann, *Ber.*, **27**, 102 (1894); Ann., **317**, 27 (1901); *Ber.*, 55,2488 (1922).

(2) The following are a few of the pertinent references: (a) Willstätter and Bommer, Ann.. **422**, 15 (1921); (b) Ruzicka and others, *Helv. Chim. Acta*, **3**, 816 (1920); **5**, 717 (1922) (c) McElvain and Adams, THIS JOURNAL, 45,2738 (1923); (d) Clemo and Ramage, *J. Chem. Soc.*, 441 (1931).

(3) McElvain and others, (a) THIS JOURNAL, **46**, 1721 (1924); (b) 48.2179 (1926); (c) 49, 2862 (1927); (d) 52,2692 (1931).

(4) DeMouilipied [*J. Chem. Soc.*, 87, 442 (1905)] reported the preparation of 1-phenyl-2 or 4-carbethoxy-3-pyrrolidone by a similar condensation. Ruzicka and Seidel [*Helv. Chim. Acta*, **5**, 516 (1922)], however, were unable to isolate a pyrrolidone derivative from an attempted internal condensation of β-carbethoxyethylcarbethoxymethylamine by means of sodium.

(5) Snell and McElvain, THIS JOURNAL, **53**, 2312 (1931).

methylamines are given in the experimental part of the paper. A summary of the reaction conditions and the results of the condensation of these esters with sodium ethoxide are given in Table I. Except in the case of run 7 (see footnote *f*, Table I), the yield of cyclic condensation product given in the sixth column represents the intramolecular condensation product, i. *e.*, the recrystallized hydrochloride of the cyclic amino-β-keto ester which was extractable by ether after the reaction mixture had been acidified with hydrochloric acid and then neutralized with potassium carbonate.[6] The reaction time in the last column of Table I shows the time necessary to obtain the yield of alcohol given in the fifth column.

TABLE I

CONDENSATION OF THE DI-ESTERS, $C_2H_5OOC(CH_2)_mN(CH_3)(CH_2)_nCOOC_2H_5$ BY SODIUM ETHOXIDE

Run	Di-ester m	Di-ester *n*	Solvent	Reaction temp., °C.[a]	Yield of C_2H_5OH, %[b]	Yield of cyclic condensation product, %	Unchanged ester recovered, %	Reaction time, hr.
1	2	2	None	120–130	78	62	0	0.33
2	2	2	Benzene	.....	84	71	0	.33
3	3	1	None	110–125	83	85	0	.33
4	2	1	None	120–130	60	36[e]	0	.33
5	2	1	Benzene	.....	85	70"	0	.33
6	4	1	Benzene	.....	Traces	0	60	20
7	4	1	Xylene[c]	.....	100	20'	0	6
8	1	1	None	120–130	55	0	0	3
9	1	1	Benzene	.....	18	0	30	20
10	4	2	Xylene[c]	.....	20	0	53	20
11	4	2	Xylene[d]	.....	65	0°	0	24
12	3	3	None	140–150	50	0	0	2
13	3	3	Benzene	.....	Traces	0	50	40
14	3	3	Xylene[c]	.....	19	0	36	24
15	3	3	Xylene[d]	.....	30	0	18	24
16	4	3	Xylene[c]	.....	3	0	55	20
17	4	3	Xylene[d]	.....	12	0	36	25
18	4	4	Xylene[d]	.....	23	0	21	40

[a] When a solvent was used the reaction temperature was the refluxing temperature of the reaction mixture. [b] Calculated on the basis of an internal acetoacetic ester condensation in which 1 mole of di-ester would produce two moles of alcohol with $NaOC_2H_5$. Obviously less alcohol would be produced if the condensation were intermolecular, e. g., two moles of di-ester would produce two moles of alcohol (50% of that produced by intramolecular condensation) if one molecule of the di-ester condensed with another. [c] In these runs a ratio of 14 g. of di-ester to 200 cc. of xylene was used. [d] A ratio of 14 g. of di-ester to 60 cc. of xylene was used. [e] Extracted with chloroform rather than ether. [f] This value represents the yield of the cyclic amino ketone (1-methyl-aza-1-cycloheptanone-3) hydrochloride rather than the yield of the cyclic amino-β-keto ester. [g] A small amount of ether extractable condensation product was obtained but hydrolysis with 20% hydrochloric acid converted it to 6-N-methylaminovaleric acid hydrochloride. Obviously it was not the expected 8-membered ring compound.

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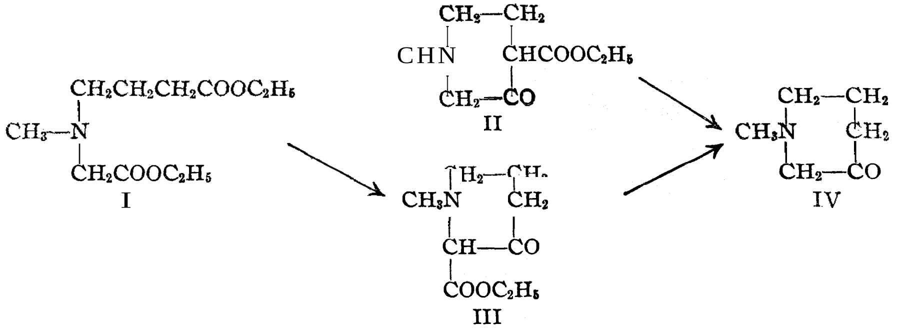
(6) The intermolecular condensation products from two or more molecules of the di-esters were not extractable from the water by ether.

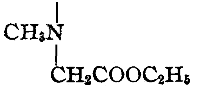
Discussion of the Results

The data obtained in runs 1 and 2 seem to justify two conclusions, (1) that sodium ethoxide is a more efficient condensing agent than metallic sodium for the formation of I-methyl-3-carbethoxy-4-piperidone (see ref. 3a for results with sodium) and *(2)* dilution of the reactants with an inert solvent favors the intramolecular condensation.

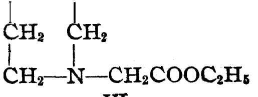
From run 3 it is seen that γ-carbethoxypropylcarbethoxymethylmethylamine (I) condenses even more readily than the isomeric β,β'-dicarbethoxydiethylmethylamine. Theoretically, the former di-ester could condense to two different 1-methylcarbethoxy-3-piperidones (II and 111), both of which, however, would be converted by hydrolysis into 1-methyl-3-piperidone (IV).



As a matter of fact a good yield of only one condensation product was obtained and it is believed that the structure of this product is given by formula II. This conclusion seems to be justified by the fact that amino di-esters which have the necessary structure (2 hydrogen atoms on an α-carbon atom) for an acetoacetic ester condensation and at the same time have an amino group attached to this a-carbon atom react very slowly, if at all, with sodium ethoxide or sodium in condensations involving this particular a-carbon atom. Runs 8 and 9 with dicarbethoxydimethylmethylamine (V) illustrate this behavior. Also it has been found[7] that ethyl (3-carbethoxypiperidino)-acetate (VI) was recovered for the most part unchanged after refluxing with either sodium ethoxide or metallic sodium in benzene, toluene, xylene or cymene solutions. Obviously the formation of structure (III) would involve condensation through an a-carbon atom carrying an amino substituent. Since the condensation took place so readily (85% in twenty minutes) it seems likely that the alternative structure (II) was formed.


$CH_3N(CH_2COOC_2H_5)_2$

V



VI

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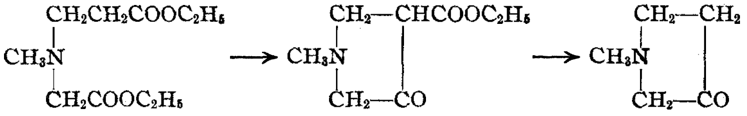
(7) McElvain and Adams, THIS JOURNAL, 46,2746 (1923).

The keto ester (II) was hydrolyzed readily into 1-methyl-3-piperidone (IV). These compounds (II and IV) are the first examples of a 3-piperidone to be prepared.* The 1-methyl-3-piperidone differs quite markedly from the isomeric 4-piperidone in that it is extremely easily oxidized, even by air, and reduces both ammoniacal silver nitrate and Fehling's solution immediately in the cold. In fact it shows the characteristic properties of an a-amino ketone.[9]

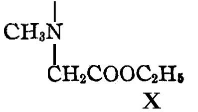
For the reason given above it is believed that β-carbethoxyethylcarbethoxymethylmethylamine VII (runs 4 and 5) condensed to 1-methyl-4-carbethoxy-3-pyrrolidone VIII, since only a single compound was obtained from the reaction. This latter compound was readily hydrolyzed to the corresponding pyrrolidone (IX). This compound, on account of its a-amino ketone structure, showed the same susceptibility to oxidation as the 1-methyl-3-piperidone.



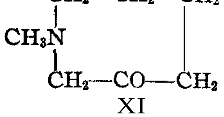
VII VIII IX

It should be noted that in this case dilution of the reactants with an inert solvent (run 5) was decidedly favorable for intramolecular condensation.

With 6-carbethoxybutylcarbethoxymethylmethylamine (X) the time for the formation of *a* substantial yield of alcohol begins to increase. The hydrochloride of the condensation product which was isolated directly from the reaction could not be caused to crystallize. This may have been due to the presence of both of the possible isomeric β-keto esters, since the conditions and time of reaction were perhaps sufficiently strenuous and prolonged in run 7 to have caused some condensation on the α-carbon atom attached to the amino group. Since both of these isomeric β-keto esters would be converted to the same cyclic ketone, the reaction product was hydrolyzed and the hydrochloride of 1-methyl-aza-1-cycloheptanone-3 (XI) isolated. This seven-membered heterocyclic ring structure is of interest in connection with the recent synthesis of a bicyclic analog, N-methyl-homogranatonine,[10] and the suggested seven-membered nitrogen ring structure for lobinine.[11]



X



XI

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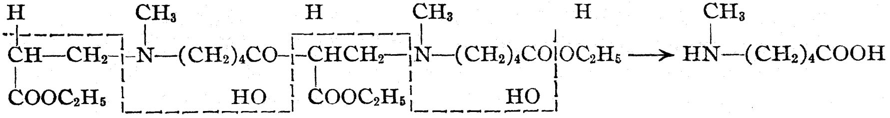
(8) Clerno and Ramage[2d] recently reported the preparation of a bicyclic analog of 3-piperidone. ethyl 1-keto-octahydropyridocoline-2-carboxylate.

(9) Cf. Beilstein, "Handbuch der organ. Chem.," 1922, Vol. IV, pp. 314, 316.

(10) Blount and Robinson, *J. Chem. Soc.*, 1429 (1932).

(11) Wieland, Ishimasa and Koschara, *Ann.*, 491, 14 (1931).

The behavior of dicarbethoxydimethylmethylamine (runs 8 and 9) has been referred to above. β-Carbethoxyethyl-δ-carbethoxybutylmethylamine which should have produced an eight-membered ring showed very little reaction in dilute xylene solution (run 10) after twenty hours. However, in more concentrated xylene solution (run 11) the higher yield of alcohol suggests an intermolecular condensation. The ether extraction for the intramolecular condensation product yielded a small amount (about 3% yield calculated as the expected cyclic β-keto ester) of material which gave a definite coloration with ferric chloride and which was converted by hydrolysis with 20% hydrochloric acid into the hydrochloride of δ-N-methylaminovaleric acid (see footnote g, Table I). This latter product undoubtedly resulted from the deamination[12] during hydrolysis of a small amount of an intermolecular condensation product which had been extracted by the ether. To illustrate with the simplest example



$$\underset{COOC_2H_5}{\overset{H}{CH}}-CH_2-\overset{CH_3}{N}-(CH_2)_4CO-\underset{HO}{}\underset{COOC_2H_5}{\overset{H}{C}}HCH_2-\overset{CH_3}{N}-(CH_2)_4CO\underset{HO}{}\overset{H}{}OC_2H_5 \longrightarrow \overset{CH_3}{HN}-(CH_2)_4COOH$$

It is seen from Table I that none of the di-esters higher than δ-carbethoxybutylcarbethoxymethylmethylamine ($m = 4$, $n = 1$) give isolable quantities of intramolecular condensation products. It should be pointed out in this connection that Littmann and Marvel[13] obtained an eight-membered cyclic quaternary salt from ω-bromoheptyldimethylamine. However, while ε-aminocaproic acid is partially converted to the seven-membered cyclic lactam structure, ζ-aminoheptanoic acid gives none of the eight-membered cyclic lactam, but only open-chain polyamides.[14]

Experimental

Materials Used

ω-Halogen Esters.—Ethyl chloroacetate was prepared by esterification of chloroacetic acid. Ethyl β-bromopropionate was prepared from ethylene cyanohydrin.[15] γ-Bromobutyric acid was prepared by the hydrolysis of γ-bromobutyronitrile[16] with 48% hydrobromic acid and esterified by the procedure described for ethyl β-bromopropionate.[15] The yield of ethyl γ-bromobutyrate from the bromonitrile was 72% of the theoretical. This ester has not been described previously in the literature. It boils at 104–105° (28 mm.); n^{25}_{D} 1.4539; d^{25}_{25} 1.3531; M_D calcd., 39.33, found, 39.14. *Anal.* Calcd. for $C_6H_{11}O_2Br$: Br, 41.00. Found: Br, 41.03. Ethyl δ-bromovalerate was prepared from δ-bromovaleric acid[17] by the esterification procedure[15] used above. This ester has been prepared previously.[17]

ω-(N-Methylamino) Esters.—Ethyl N-methylaminoacetate (sarcosine ester)

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[12] Cf. Thomas and McElvain, THIS JOURNAL, 54, 3295 (1932).

[13] Littmann and Marvel, *ibid.*, 52, 287 (1930).

[14] Carothers and Berchet, *ibid.*, 52, 5289 (1930).

[15] "Organic Syntheses," 1923, Vol. III, p. 51.

[16] Derick and Hess, THIS JOURNAL, 40, 547 (1918).

[17] Merchant, Wickert and Marvel, *ibid.*, 49, 1828 (1927).

hydrochloride was prepared by the alcoholysis of methylaminoacetonitrile[18] by the procedure described by Staudt.[19] The ethyl N-methylaminoacetate hydrochloride after recrystallization from chloroform melted at 126–127°.[20] The free amino ester, ethyl N-methylaminoacetate, was liberated from its hydrochloride just before it was used by the following method. A suspension of the hydrochloride in *dry* ether was treated with *dry* ammonia gas until all of the particles of the hydrochloride appeared to be replaced by the very finely divided precipitate of ammonium chloride. This precipitate was filtered off, suspended in a fresh portion of ether, and again treated with ammonia. After filtration these ethereal solutions were combined and, after removal of the ether, the amino ester was distilled. It boiled at 59–60° (25 mm.) and the recovery from the hydrochloride amounted to 90% of the theoretical.

Ethyl β-N-methylaminopropionate was prepared by a method previously described.[21] This amino ester could be converted into a crystalline hydrochloride, m. p. 59–60°.

Anal. Calcd. for $C_6H_{14}O_2NCl$: Cl, 21.16. Found: 20.99.

Ethyl δ-N-methyl aminovalerate was prepared in the following manner, 1-Methyl-2-pyridone[22] was hydrogenated over nickel to 1-methyl-2-piperidone.'' The yield of product boiling at 97–98' (11 mm.) was practically quantitative. This piperidone gives a hygroscopic hydrochloride, m. p. 104–105°.[24] To 57 g. of this piperidone was added a solution of 40 g. of sodium hydroxide in 100 cc. of water and this solution refluxed for one hour. After cooling 150 cc. of concentrated hydrochloric acid was added and the solution evaporated to dryness under diminished pressure. The residue was extracted with 150 cc. of boiling absolute alcohol and the insoluble sodium chloride removed by filtration. To the alcoholic solution was added 300 cc. of absolute alcohol containing 10% dry hydrogen chloride. This solution was refluxed for eight hours and then evaporated to dryness under diminished pressure. To complete the esterification the residue was refluxed for an additional eight hours with another 400-cc. portion of absolute alcohol containing 6% of dry hydrogen chloride. On evaporation of this solution under diminished pressure a residue of ethyl 6-N-methylaminovalerate hydrochloride remained which after recrystallization from ethyl acetate melted at 108–109.

Anal. Calcd. for $C_8H_{18}O_2NCl$: Cl, 18.13. Found: Cl, 18.07.

The free amino ester was liberated from this hydrochloride in the same manner as described above for ethyl-N-methylaminoacetate. The ethereal solution of the free amino ester was freed from the ether by distillation and the higher boiling residue used directly in the subsequent experiments. Distillation of this residue of free amino ester caused a considerable amount of it to be converted into the original lactam, 1-methyl-2-piperidone. Also, standing at room temperature caused this amino ester to change into the lactam and alcohol. For this reason no analyses or determinations of physical properties were made.

ω,ω′-Dicarbethoxydialkylmethylamines.—β,β′-Dicarbethoxydiethylmethylamine was prepared from ethyl β-bromopropionate and methylamine by a procedure pre-

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(18) Biltz and Slotta, *J. prakt. Chem.*, [2] *113*, 252 (1926).

(19) Staudt, *Z. physiol. Chem.*, 146,286 (1925).

(20) *Cf.* Sigmund and I iedl, *ibid.*. **202**, 268 (1931).

(21) McElvain, THIS JOURNAL, **46**, 1726 (1924).

(22) Decker, *J. prakt. Chem.*, [2] **47**, 28, 222 (1893); *ibid.*, [2] **84**, 219, 432 (1911). This procedure involves the oxidation of pyridine methosulfate with potassium ferricyanide. It was found advantageous to modify this procedure at two points. First, the order of addition of reactants was reversed, *i. e.*, the ferricyanide and alkali solutions were slowly added to the solution of the pyridine methosulfate. Second, amyl alcohol was used to extract the pyridone instead of benzene since it was found that benzene failed to dissolve the pyridone hydrate, a form in which considerable of the pyridone is present.

(23) Covert, Connor and Adkins, THIS JOURNAL, **54**, 1658, 1661 (1932).

(24) *Cf.* Rath, Ann., **489**, 113 (1931).

viously described.[25] γ,γ′-Dicarbethoxydipropylmethylamine was likewise prepared from methylamine and ethyl γ-bromobutyrate, but it was necessary to use the following procedure on account of the lower reactivity[26] of this bromo ester. A solution of 60 g, (0.3 mole) of ethyl γ-bromobutyrate in 50 cc. of absolute alcohol was refluxed gently in a 1-liter flask fitted with a reflux condenser and a dropping funnel. To this boiling solution a solution of 16 g. (0.5 mole) of methylamine in 150 cc. of absolute alcohol was added slowly over a period of four hours. The solution was then refluxed for an additional four hours. Then about 100 cc. of alcohol was distilled out and on cooling a crop of methylamine hydrobromide crystals which separated was filtered off. The remaining alcohol was removed under diminished pressure. The residue was treated with 50-cc of water and sufficient hydrochloric acid to give a distinct acid reaction to Congo red. The unreacted bromo ester was then extracted with ether, after which the aqueous solution was neutralized with potassium carbonate and the γ,γ′-dicarbethoxydipropylmethylamine extracted with petroleum ether. After removal of this solvent under diminished pressure, 6 g. of the tertiary amino ester boiling at 162–166° (14 mm.) was obtained. The aqueous layer was further extracted with chloroform and this extract distilled. After removal of the chloroform, 6 g. of 1-methyl-2-pyrrolidone,[27] b. p. 82–87° (14 mm.) and 5 g. of a fraction boiling at 115–170° (14 mm.) were obtained This latter fraction was dissolved in petroleum ether and shaken with several portions of water to remove any of the pyrrolidone. This petroleum ether extract on distillation yielded an additional 2 g. of γ,γ′-dicarbethoxydipropylmethylamine, b. p. 162–166° (14 mm.) The total yield was therefore 8 g. or 20% of the theoretical.

The remainder of the ω,ω′-dicarbethoxydialkylmethylamines were prepared by the interaction of 1 mole of an ω-halogen ester and 2 moles of an ω-N-methylamino ester (see Table II). The reactants were mixed and allowed to stand from four to twenty-four hours at room temperature, after which time the reaction mixture was diluted with ether. The secondary amino ester hydrohalide which precipitated was separated from the ethereal solution and then the latter was distilled. In those cases when ethyl δ-N-methylaminovalerate was used a considerable amount of 1-methyl-2-piperidone was formed in the reaction.

All of these tertiary amino esters before use were subjected to the following general method of purification. After fractionation at the time they were prepared, they were allowed to stand in stoppered bottles for a month or more. During this time any halogen ester which might be present reacted with the tertiary amine and any unchanged secondary amino ester reacted with itself to form a lactam, a diketopiperazine, or an open chain condensation product. The product was then dissolved in ten times its volume of petroleum ether and shaken with several small portions of water in order to remove any of these secondary reaction products, all of which are preferentially dissolved in the water layer. The petroleum ether solution was then dried over anhydrous sodium sulfate and, after removal of the solvent, the product was distilled. There was very little loss resulting from this purification process.

Table II gives the data concerning the preparation, properties and analyses of these tertiary amino esters.

The Condensation of ω,ω′-Dicarbethoxydialkylmethylamines by Sodium Ethoxide. I. Without a Solvent.—One mole of the di-ester and 1 mole of sodium ethoxide were mixed in a distilling flask fitted with a mercury-sealed stirrer and a condenser set for downward distillation. A tared receiver, protected by a soda lime tube, was attached to the condenser. With the stirrer in operation the flask was immersed in an oil-bath and

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(25) McElvain, THIS JOURNAL, 46, 1724 (1924); Bolyard, University of Wisconsin, Ph.D. Thesis, 1928.

(26) *Cf.* Wohlgemuth, *Ann. Chim.*, 2, 314 (1914).

(27) Tafel and Wassmuth, *Ber.*, 40, 2836 (1907); Gansser, *Z. physiol.* Chem., 61, 59 (1909).

heated to the temperature indicated in Table I. The reaction was continued until no more alcohol distilled out.

TABLE II

ω,ω′-DICARBETHOXYDIALKYLMETHYLAMINES, $C_2H_5OOC(CH_2)_mN(CH_3)(CH_2)_nCOOC_2H_5$

m	n	Formula	$H—N(CH_2)_mR^a—CH_3$ used[d] m is	Yield,[e] %	B. p., °C. (mm.)	d_{25}^{25}	n_{D}^{25}	M_D Calcd.	M_D Found	Analyses, N, % Calcd.	Analyses, N, % Found
2	2[b]	$C_{11}H_{21}O_4N$	.	70	134–135 (10)	....	....	...	...	..	..
3	3[c]	$C_{13}H_{25}O_4N$	.	20	159–160 (9)	0.9913	1.4407	69.48	69.19	5.40	5.37
1	1	$C_9H_{17}O_4N$	1	75	114–115 (11)	1.0485	1.4328	51.01	50.48	6.89	6.91
1	2	$C_{10}H_{19}O_4N$	1	85	124–125 (10)	1.0287	1.4350	55.63	55.13	6.45	6.48
1	3	$C_{11}H_{21}O_4N$	1	80	134–135 (10)	1.0145	1.4367	60.25	59.85	6.05	5.90
4	1	$C_{12}H_{23}O_4N$	4	73	146–147 (9)	1.0032	1.4393	64.86	64.78	5.71	5.64
4	2	$C_{13}H_{25}O_4N$	4	54	159–160 (9)	0.9914	1.4410	69.48	69.26	5.40	5.38
4	3	$C_{14}H_{27}O_4N$	4	58	166–167 (9)	.9814	1.4420	74.10	73.89	5.12	5.11
4	4	$C_{15}H_{29}O_4N$	4	55	177–178 (9)	.9741	1.4438	78.72	78.55	4.87	4.81

[a] R = $COOC_2H_5$. [b] This compound has been described previously.[25] [c] This ester was prepared from methylamine and $Br(CH_2)_3COOC_2H_5$. [d] The halogen ester, $X(CH_2)_nCOOC_2H_5$ reacts with this secondary amino ester in the cases where the latter is used. [e] Of tertiary amino ester and based on amount of ω-halogen ester used in the reaction.

II. Benzene as a Solvent.—A three-necked flask of suitable size was fitted with a mercury seal stirrer and a Vigreaux fractionating column surrounded by a jacket. By filling this jacket with water the column could be used as a reflux condenser. A thermometer was inserted in the head of the column and the side arm attached to a condenser set for downward distillation. A solution of 30–40 g. of the di-ester in 250 cc. of benzene and the theoretical amount of sodium ethoxide were then added through the third neck of the reaction flask. The flask was then heated in an oil-bath with the jacket of the column empty until the azeotropic mixture of alcohol and benzene distilled out and the thermometer reached the boiling point of benzene. Then water was circulated through the jacket for a few minutes, after which the water again was run out and the distillation carried out as before. This process was repeated until the distillate showed the refractive index of pure benzene. The amount of alcohol in the distillate was determined from its refractive index. Most of the benzene was then removed from the residue in the reaction flask by distillation and about 120 cc. of water added, and the amino-β-keto ester isolated as the hydrochloride by the procedure previously described.[3a]

III. Xylene as a Solvent.—The same apparatus was used as when benzene was the solvent except that the column was not surrounded by a jacket. The ratio of reactant to solvent is given in Table I, footnotes *c* and d. The reaction flask was heated in an oil-bath sufficiently to cause gentle refluxing from the column. Periodically the temperature of the bath was raised and the mixture of alcohol and xylene distilled out until the thermometer registered the boiling point of xylene. When no more alcohol came over the remaining xylene was removed under diminished pressure from the reaction mixture. The seven membered cyclic amino-β-keto ester was found to differ from its 5 and 6 membered ring analogs in that it was extractable by ether from an aqueous solution of its sodium derivative. Consequently the extraction for the cyclic β-keto ester was made after the reaction mixture had been treated with water. When such an extraction was carried out until the ether extracts showed no coloration with ferric chloride. treatment of the remaining aqueous solution by the usual isolation procedure[3a] yielded no additional condensation product. The alcohol in the distillate was determined by the phthalic anhydride method.[5] The properties and analyses of the new cyclic amino-β-keto ester hydrochlorides isolated in the present work are given in Table III.

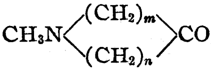
TABLE III

CYCLIC AMINO-β-KETO ESTER HYDROCHLORIDES

Compound, hydrochloride	Formula	M. p., °C.	Analyses, % Calcd. C	H	Cl	Found C	H	Cl
1-Methyl-4-carbethoxy-3-piperidone	$C_9H_{16}O_3NCl$	171–173 (decomp.)	48.82	7.27	16.00	48.51	7.21	15.98
1-Methyl-4-carbethoxy-3-pyrrolidone	$C_8H_{14}O_3NCl$	132–133	46.24	6.80	17.09	45.33	6.93	17.35

The β-keto esters of Table III as well as the uncrystallizable β-keto ester resulting from the intramolecular condensation of δ-carbethoxybutylcarbethoxymethylmethylamine were hydrolyzed by refluxing in dilute hydrochloric acid until the solution showed no coloration with ferric chloride. Evaporation of this acid solution left the hydrochloride of the corresponding ketone, which was recrystallized from dry acetone. In certain cases the free bases were prepared from the hydrochlorides. These compounds are summarized in Table IV. For comparison some of the properties of the corresponding 2-pyrrolidone and the 2- and 4-piperidones are included in this table.

TABLE IV

CYCLIC AMINO KETONES, 

$CH_3N\begin{smallmatrix}(CH_2)_m\\(CH_2)_n\end{smallmatrix}CO$, AND THEIR HYDROCHLORIDES

m	n	B. p., °C. (mm.)	d^{25}_{25}	n^{25}_D	M_D Calcd.	M_D Found	Analyses, N, % Calcd.	Analyses, N, % Found	Hydrochloride, m. p., °C.	Hydrochloride analyses, Cl, % Calcd.	Hydrochloride analyses, Cl, % Found
2	1	46–47 (18)	0.9675	1.4431	27.04	27.23	14.13	14.06	62– 63	26.17	24.50[a]
3	0[b]	84–85 (14)	1.0260	1.4666	27.04	26.86	...	...	79– 81	26.17	25.89
2	2[c]	56–58 (11)	0.9725	1.4580	31.66	31.83	12.38	12.31	94– 95[c]	...	...
3	1	63–64 (13)	.9684	1.4559	31.66	31.64	12.38	12.40	110–111	23.71	23.52
4	0	97–98 (11)[d]	1.0293	1.4801	31.66	31.31	...	...	104–105[e]	...	...
4	1	... ..	....	....	...	...	...	...	195–196	21.68	21.46[f]

[a] Low analyses in this case are probably due to solvent of crystallization, *cf.* Bolyard and McElvain, THIS JOURNAL, 51,924 (1929). [b] Cf. Ref. 27. [c] The hydrochloride of this ketone has been described (see ref. in footnote *a*), but the free ketone was not isolated. [d] *Cf.* Ruzicka, *Helv. Chim. Acta*, *4*, 474 (1921). [e] *Cf.* Ref. 24. [f] Additional Anal. Calcd.: C, 51.34; H, 8.63. Found: C, 51.28; H, 8.75.

Summary

A series of ω,ω'-dicarbethoxydialkylmethylamines, $C_2H_5OOC(CH_2)_m$-$N(CH_3)(CH_2)_nCOOC_2H_5$, in which both *m* and *n* are varied from 1 to 4, have been prepared and their cyclization through an internal acetoacetic ester condensation under a variety of conditions has been studied.

Derivatives of 3-pyrrolidone, 3- and 4-piperidone, and aza-1-cycloheptanone-3 have resulted from the intramolecular condensation of certain of these di-esters. With the other di-esters of the series the condensation, as judged by the amount of alcohol given off, was quite slow and incomplete and went to give intermolecular condensation products.

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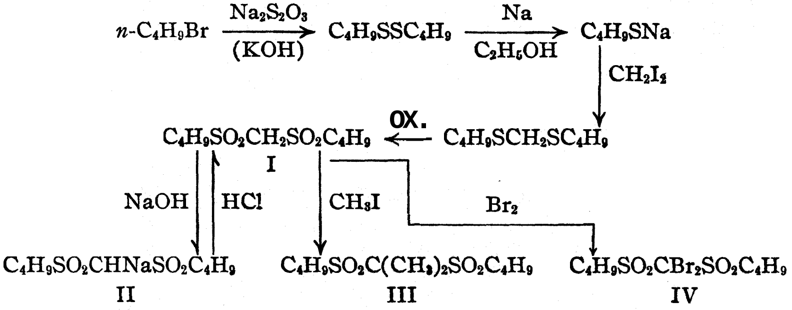
The Preparation and Properties of Methylene Di-n-butyl Disulfone

BY R. E. STUTZ AND R. L. SHRINER

Methylene diphenyl disulfone has been found to be easily alkylated and readily soluble in aqueous sodium hydroxide.[1] The activity of the methylene group in this compound was greater than that of a methylene group in 1,3-diketones and appeared to be due to the fact that it is situated between two sulfonyl groups. However, the two phenyl radicals may also have had some activating influence. Hence, it was desirable to study a compound in which the phenyl radicals had been replaced by alkyl groups. The following chart (I) summarizes the preparation and reactions of such a compound, namely, methylene di-n-butyl disulfone.

CHART I



Methylene di-n-butyl disulfone (I) was found to be soluble in dilute sodium hydroxide solution yielding the salt (II) and upon acidification the original compound (I) was obtained. It was readily alkylated to the disubstituted product III which was alkali insoluble. Bromination produced the bromo derivative IV. The bromine in this compound liberated iodine from potassium iodide solution. These properties show the methylene group to be unusually active. Since the properties of this disulfone parallel those of methylene diphenyl disulfone it seems probable that the methylene group owes its reactivity to the two sulfonyl groups and that the other radicals attached to the sulfur atom have negligible influence. The properties of this disulfone constitute further experimental evidence in favor of the structure of sulfones and their salts previously discussed.[1]

The synthetic procedure outlined in Chart I was unique in that it avoided the preparation of the disagreeable mercaptans. The reaction[2] between n-butyl bromide, alcoholic sodium thiosulfate and potassium hydroxide proceeded smoothly to give 44–47% yields of dibutyl disulfide which was

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(1) Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

(2) Spring and Legros, *Ber.*, **15**, 1938 (1882); Price and Twiss, *J. Chem. Soc.*, **93**, 1395 (1908).

reduced to the sodium mercaptide by sodium and alcohol. The solution of the mercaptide was used directly for the reaction with methylene iodide.

It has also been found that organic disulfides dissolved in toluene or xylene may be cleaved by sodium[3] or sodium--potassium alloy to the metal alkyl or aryl mercaptide which may be readily characterized by condensation with 2,4-dinitrochlorobenzene.[4] The yields of metal mercaptides obtained by direct cleavage were lower than by reduction with sodium and alcohol, but either method now affords a means of preparing various types of mixed thioethers without the necessity of working with the very disagreeable mercaptans. From these thioethers in turn many interesting compounds may be made. The reactions which lead to the methylated sulfone (III) constitute a new method for the synthesis of homologs of sulfonal.

Experimental

Di-*n*-butyl Disulfide.—To 137 g. of n-butyl bromide and 500 cc. of alcohol in a 2-liter three-necked flask fitted with a mercury-sealed stirrer was added 300 *g.* of sodium thiosulfate dissolved in 400 cc. of water and the mixture refluxed for one and one-half hours. Then 140 g. of potassium hydroxide in 300 cc. of water was added and the mixture again heated for half an hour. The disulfide separated as an oil and the alkali sulfate and sulfite salts precipitated. The di-n-butyl disulfide after extraction with ether was distilled and collected at 120–123° under 25–30 mm.; yield. 42 g. (47%) of a slightly yellow liquid,[5] b. p. 226° at 760 mm.; d^{20}_{20} 0.944, n^{20}_{D} 1.4926; M_D calcd., 55.38; found, 54.90.

Methylene **Di-*n*-butyl Disulfide.**—To 50 *g.* of di-n-butyl disulfide in 800 cc. of absolute alcohol, in a 2-liter three-necked flask equipped with a mercury-sealed stirrer and reflux condenser, was added 40 g. of sodium. After the sodium had dissolved, 21 cc. fo water was added to react with the excess sodium ethylate.

The stirrer was started and 77 g. of methylene iodide added slowly (one hour). The mixture was refluxed with stirring for three hours. Three 200-cc. portions of alcohol were distilled from the solution and replaced with water. The product was extracted with ether and distilled: b. p. 133–138° at 30–35 mm. (b. p. 250° at 760 mm.); yield, 44 *g.* (82%); d^{20}_{20} 0.947; n^{20}_{D} 1.4946; M_D calcd., 59.72; found, M_D, 59.26.

Anal. Calcd. for $C_9H_{20}S_2$: S, 33.35. Found: S, 33.11.

Methylene **Di-*n*-butyl Disulfone.**—To 27.6 g. of methylene di-n-butyl disulfide in 200 cc. of glacial acetic acid, 84 g. of chromium trioxide was added over a period of one and one-half hours. The flask was warmed at first, but later the reaction proceeded smoothly without further heating. After the reaction had stopped the mixture was poured on crushed ice, filtered and purified by recrystallizing twice from water, and once from absolute alcohol; m. p. 95–96"; yield 4.7 g. or 13%. The product readily dissolved in 5% aqueous sodium hydroxide and was precipitated by hydrochloric acid.

Anal. Calcd. for $C_9H_{20}O_4S_2$: S.25.00. Found: S, 24.69.

A compound described *as* methylene di-n-butyl disulfone with a melting point of 182° has been previously mentioned by Whitner and Reid,[6] who prepared it by oxidizing the disulfide with sodium dichromate and sulfuric acid or with fuming nitric acid. The preparation of the disulfone was repeated using the dichromate oxidation and the prod-

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(3) **Lecher,** *Ber.*, 48, 524 (1915); 48, 1425 (1915); 66, 577 (1920).

(4) **Bost, Turner and Norton,** THIS JOURNAL, 64, 1985 (1932).

(5) **Hunter and Sorenson,** *ibid.*. 64, 3366 (1932).

(6) **Whitner and Reid,** *ibid.*, 48, 638 (1921).

uct found to melt at 95–96°. An attempted oxidation by means of fuming nitric acid resulted in a violent reaction from which nothing could be isolated. Moreover, Stuffer[7] found the melting point of methylene di-isobutyl disulfone to be 85° and Posner[8] found 138–139° for methylene diamyl disulfone. The melting point for the di-n-butyl compound (95–96°) falls between these values as would be expected.

Bromination of Methylene Di-*n*-butyl Disulfone.—To 0.2 g. of methylene di-*n*-butyl disulfone dissolved in 600 cc. of hot water was added 0.5 g. of bromine and the mixture warmed on the steam cone for two hours. The solution was then cooled in ice and the colorless needle-like crystals filtered and recrystallized from absolute alcohol; m. p. 80°, yield, 0.15 g. or 47%.

Anal. Calcd. for $C_9H_{18}O_4S_2Br_2$: Br, 38.59. Found: Br. 38.56.

Alkylation of Methylene Di-*n*-butyl Disulfone.—To a solution of 0.15 g. of sodium in 100 cc. of absolute alcohol was added 0.85 g. of methylene di-n-butyl disulfone. Next 1 cc. of methyl iodide was added and the mixture refluxed for 2.25 hours. Fifty cubic centimeters of alcohol was distilled from the flask and the residue poured on crushed ice. The product was filtered by suction and recrystallized from ligroin; colorless needles; m. p. 67–68°; mixed melting point with the original disulfone (m. p. 95-96°), 54-57°; yield, about 0.4 g or 40%. The product was insoluble in aqueous alkalies.

Anal. Calcd. for $C_{11}H_{24}O_4S_2$: S, 22.55. Found: S, 22.65.

Cleavage **of Di-*n*-butyl Disulfide.**—The rupture at the sulfur–sulfur linkage in disulfides may also be brought about in the following manner.

A. With Metallic Sodium.—One and twenty-five hundredths grams of metallic sodium was added to 100 cc. of dry xylene contained in a 200-cc. round-bottomed flask equipped with a reflux condenser. Five gram.; of di-n-butyl disulfide was added and the mixture heated on the steam cone for twelve hours. The product was filtered and washed with absolute ether. Following the method suggested by Bost, Turner and Norton[4] the mercaptide was then converted to the 2,4-dinitrophenyl thioether, which was obtained as yellow needles; m. p. 66° (m. p. lit. 66°); yield 6 g. or 42%.

B. With Sodium–Potassium Alloy.—The sodium–potassium alloy was prepared by adding 1.05 g. of potassium and 0.62 g. of sodium to 100 cc. of dry xylene and then heating until alloyed. Five grams (slight excess) of di-n-butyl disulfide was then added to the hot liquid alloy and the mixture allowed to stand overnight. To ensure complete reaction with the metal, the mixture was heated for several hours on the steam cone. The mixed mercaptide thus formed was likewise purified and characterized as the 2,4-dinitrophenyl thioether, giving yellow needles; m. p. 66°, yield 6.5 g. or 45%.

Cleavage of Diphenyl Disulfide

A. With Powdered Metallic Sodium.—Five grams of diphenyl disulfide was treated with 1.05 g. of sodium in xylene as above. In this case, however, the metal was first reduced to a powder. The reaction rate was noticeably increased; yellow needles of the 2,4-dinitrophenyl thioether were obtained; m. p. 121° (m. p. recorded, 121°), yield 5.5 g. or 44%.

B. With Sodium–Potassium Alloy.—The alloy was prepared as above. Five grams of diphenyl disulfide, 0.52 g. of sodium and 88 g. of potassium gave a product which when treated with 2,4-dinitrochlorobenzene gave yellow needles; m. p. 121°; yield 7.5 g. or 60%.

Summary

Methylene di-n-butyl disulfone has been prepared and found to be soluble in aqueous alkalies, easily brominated and readily alkylated.

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(7) Stuffer, *Ber.*, 23, 3230 (1890).

(8) Posner, *ibid.*, 86, 296 (1903).

Sodium or sodium–potassium alloy cleaved alkyl and aryl disulfides to the metal mercaptides.

URBANA, ILLINOIS

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The Action of Alkalies on the Monobasic Sugar Acids.[1] I. Conversion of Gluconic to Mannonic and of Galactonic to Talonic Acids by the Action of Barium Hydroxide

BY HOWARD T. BONNETT AND FRED W. UPSON

This paper records experiments on the action of barium hydroxide on several monobasic sugar acids. It has been found that epimerization of these acids may be produced by the action of barium hydroxide and that the action of pyridine, quinoline and other tertiary amines is not specific in this process. Thus, *d*-gluconic acid has been converted to d-mannonic acid, d-mannonic to d-gluconic, and d-galactonic to d-talonic acid. The mannonic and talonic acids have been isolated in the form of their γ-lactones.

The preparation of *d*-mannonic acid by the epimerization of d-gluconic acid was discovered by Fischer[2] and recently Nelson and Cretcher[3] have described its preparation from ivory-nut meal.

d-Talonic acid was prepared from d-galactonic acid by Fischer,[4] and Cretcher[5] has recently published an improved method.

That barium hydroxide is capable of producing epimeric change is of interest in connection with the general problem of the oxidation of sugars in alkaline solution. Thus in the oxidation of glucose by Fehling's solution[6] and by the Soldaini reagent,[7] mannonic acid or a derivative has been isolated as one product, and gluconic acid has been obtained in the oxidation of mannose.[8] In like manner d-talonic acid was found as an oxidation product of galactose in the work of Anderson.[9] Nef[8] and also Anderson[9] explained the formation of the isomeric hexonic acid in the oxidation of a given hexose, as the result of a benzilic acid rearrangement of the 1,2-osone, formed by the oxidation of the 1,2-enediol of the hexose. Jensen and Upson[10] suggested that an alternative explanation is to be

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(1) An abstract of a part of a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Nebraska.

(2) Fischer, Bar., 43, 799 (1890).

(3) Nelson and Cretcher, THIS JOURNAL, 52, 403 (1930).

(4) Fischer, *Ber.*, 44, 3622, 3629 (1891).

(5) Cretcher, Tars JOURNAL, 49, 478 (1927); 54, 1590 (1932).

(6) Nef, *Ann.*, 357, 276 (1907).

(7) Jensen and Upson, Tars JOURNAL, 47, 3019 (1925).

(8) Nef, *Ann.*, 357, 281 (1907).

(9) Anderson, *Am. Chem. J.*, 44, 402 (1909).

(10) Jensen and Upson, THIS JOURNAL, 47, 3024 (1925).

found in the well-known Lobry de Bruyn–van Ekenstein[11] reaction. Through the action of the alkali a given hexose may be converted to its isomeric sugar which then undergoes direct oxidation to the corresponding hexonic acid.

The experiments presented in this paper suggest a third possible mechanism. Since the Fehling's solution reactions are usually carried out at temperatures of 100°, it is entirely possible that the mannonic acid recovered in the oxidation of glucose results, in part at least, from the epimerization of gluconic acid through action of the alkali. The same theory would account for the formation of gluconic acid in the oxidation of mannose and of talonic acid in the oxidation of galactose.

It is not possible with the evidence at hand to decide between the three possible mechanisms. Any one may be, or possibly all three are, involved in the formation of the isomeric hexonic acid in the oxidation of a given hexose.

Experimental

Preparation of γ-*d*-Mannonic Lactone.—282 g. of barium gluconate and 158 g. of barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) were dissolved in water in a one-liter round-bottomed flask with the aid of heat, and the volume made up to 1 liter. The flask was stoppered and maintained at a temperature of 95–97° for one hundred and fifteen hours. The hot solution was neutralized to litmus with 6 *N* sulfuric acid and the barium sulfate removed by filtration. The resulting solution was concentrated to 600 cc. and allowed to stand for twenty-four hours in a refrigerator. The barium gluconate which separated was filtered out and washed with ice water. The combined filtrate and washings was concentrated to 200 cc. and a second crop of barium gluconate removed in the same way. Thus there was removed 186 g. of barium gluconate or 66% of the original amount used.

The filtrate from the second crop of barium gluconate was heated and the barium ion exactly removed with sulfuric acid. After removal of the barium sulfate, the filtrate was decolorized and concentrated under reduced pressure to a thin sirup from a bath at 60°. Four hundred cc. of normal butyl alcohol and some ethyl alcohol were added to dissolve the sirup. A small amount of material remained undissolved and was filtered out. This mixture was distilled under reduced pressure from a bath maintained at a temperature of 45–50" until it became faintly turbid. It was then diluted with butyl alcohol and warmed slightly to a clear solution. It was allowed to cool to room temperature, and a few milligrams of γ-*d*-mannonic lactone added. The distillation was continued until approximately 60–70% of the butyl alcohol had been removed. During the distillation, the mannonic lactone began to crystallize. The mixture was allowed to stand at room temperature for twenty-four hours. The crystals were filtered, washed with n-butyl alcohol and dried. The yield was 30 g. (17%) of crude mannonic lactone, m. p. 147–149°. The lactone was recrystallized from ethyl alcohol and then from acetic acid for final purification; m. p. 151°, $[\alpha]^{20}_{D}$ +51.8°.

The time consumed in carrying out the preparation of γ-*d*-mannonic lactone from gluconic acid may be materially shortened if the temperature is increased. This is shown by the following experiment: 56.3 g. of barium gluconate and 31.5 g. of barium hydroxide were dissolved in hot water and diluted to 200 cc. The mixture was placed in a 200-cc. round-bottomed flask having the stopper securely wired in place, and heated

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(11) Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, 14, 201 (1895).

For one hour on an oil-bath at 140°. On removal from the bath and cooling, the mixture was treated as described above; 25.5 g. (45%) of barium gluconate was recovered and 7.3 g. (20%) of y-d-mannonic lactone was obtained.

Conversion of Mannonic to Gluconic Acid.--17.8 g. of *d*-mannonic lactone and 47 g. of barium hydroxide were dissolved in water and diluted to 200 cc. The solution was heated on a water-bath maintained at 95–97' for one hundred hours. Upon removal from the water-bath, the solution was neutralized to litmus with 6 N sulfuric acid, and the barium sulfate filtered off. The solution of barium salts was concentrated under reduced pressure to 40 cc., inoculated with barium gluconate, and placed in the refrigerator for several days. The crystals were filtered out, washed with ice cold water, and dried. The barium gluconate thus obtained weighed 3 g., corresponding to 12% of the lactone originally used.

A portion of the barium salt was used to prepare the phenylhydrazide. On recrystallization from water, the phenylhydrazide melted at 200–202°. From another portion of the barium salt, the brucine salt was prepared by the usual method. The brucine salt, dried in *vacuo* over concentrated sulfuric acid, melted at 155–157°, and gave $[\alpha]^{20}_{D}$ –18.9°. Nef[12] gives d-gluconic phenylhydrazide, m. p. 200–201°, brucine d-gluconate, m. p. 155–157°, $[\alpha]^{20}_{D}$ –18.76".

The barium ion was exactly removed from the solution of the soluble barium salt with sulfuric acid, and the barium sulfate filtered out. The filtrate was distilled, using butyl alcohol according to the method given previously under the preparation of *d*-mannonic lactone, and thus 10.8 g. (61%) of γ-*d*-mannonic lactone was recovered.

The Preparation of γ-*d*-Talonic Lactone.—98 g. of d-galactonic lactone monohydrate and 168 g. of barium hydroxide were dissolved in hot water, diluted to 500 cc. and placed in a 500-cc. round-bottomed flask. The flask was stoppered, and the mixture heated on a water-bath maintained at 95–97' for one hundred and fifty hours. Upon removal from the water-bath, the hot solution was neutralized to litmus with 6 N sulfuric acid, diluted to 3 liters, heated to boiling, and a hot solution of 105 g. of cadmium sulfate added slowly. The mixture was treated with activated charcoal and filtered while hot. The solution of the cadmium salt was concentrated under reduced pressure to 500 cc. and allowed to stand for several hours. The cadmium galactonate was filtered off, and the mixture further concentrated to 100 cc. and allowed to stand. A second small fraction of cadmium galactonate was obtained. The filtrate from the second crop of cadmium galactonate was treated with hydrogen sulfide, and the cadmium sulfide filtered out. The sulfate ion remaining in the solution was exactly removed as barium sulfate with barium hydroxide. The filtrate was concentrated *in vacuo* from a bath at 45–50° until it had reached the consistency of a thin sirup; 250 cc. of n-butyl alcohol was added, the mixture heated to a temperature of approximately 40°, and sufficient ethyl alcohol added to dissolve the sirup. A small amount of insoluble material was filtered out. The alcoholic mixture was concentrated under reduced pressure in a bath at a temperature of 45–50', to a volume of 75 cc. and allowed to stand. The gummy crystals were filtered off and recrystallized from absolute ethyl alcohol. The crystals melted at 132–134" and possessed a specific rotation of –34.5" (0.4208 g. in 19.0407 g. of water gave α = –1.49'). The weight of purified crystals was 11.4 g. (13%). These constants agree with those given by Cretcher[6] for y-d-talonic lactone.

Further studies of the action of alkalies on sugar acids are in progress.

Summary

1. It has been shown that epimerization may be produced by the action of barium hydroxide. Gluconic acid has been converted to mannonic

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(12) Nef, *Ann.*, 403, 305 (1914).

acid, mannonic acid to gluconic acid and galactonic acid to talonic acid, in yields comparable with those obtained by the use of pyridine and quinoline.

2. The process described furnishes perhaps the most convenient method for obtaining mannonic and talonic lactones.

3. A possible mechanism has been suggested for the formation of isomeric hexonic acids in the alkaline oxidation of hexoses.

LINCOLN, NEBRASKA

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

The Polymerization of Some Unsaturated Hydrocarbons. The Catalytic Action of Aluminum Chloride[1]

BY W. H. HUNTER AND R. V. YOHE

The action of aluminum chloride on unsaturated hydrocarbons has not been studied very extensively. However, as a result of a study of the action of this reagent with ethylene, Stanley[2] concluded that any explanation of the reaction must take into account the formation of an aluminum chloride–hydrocarbon complex which he has shown to lead to the formation of olefinic compounds. An earlier study with ethylene, propylene, isobutylene, n-octene and diamylene led Szayna[3] to somewhat similar conclusions. Aside from these investigations, the action of aluminum chloride on unsaturated hydrocarbons has received very little attention. Since aluminum chloride forms complexes so readily with hydrocarbons and certain other substances, it was decided to study the action of some of these complexes as polymerizing agents. The unsaturated hydrocarbons used in this study were acetylene, ethylene and isobutylene.

Preparation and Purification of Materials

Acetylene.—Tank acetylene was purified by passing it through saturated bisulfite solution, concentrated sulfuric acid, concentrated alkali, granular calcium chloride and anhydrone.

Ethylene.—Anesthesia ethylene was used without further purification.

Isobutylene.—Isobutylene was prepared by the dehydration of tertiary butyl alcohol with aluminum oxide at 400°, and also by treating tertiary butyl chloride with alcoholic potassium hydroxide. The isobutylene was washed with water, then passed over soda lime, solid sodium hydroxide, calcium chloride and anhydrone, and was finally condensed in small cylinders.

Aluminum Chloride.—Mallinckrodt anhydrous resublimed c. p. aluminum chloride was used without further purification except in the cases when it was sublimed into adsorption chambers.

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(1) The work described in this paper constituted part of a thesis submitted to the graduate Faculty of the University of Minnesota by R. V. Yohe, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. This paper was prepared by the junior author after the death of Dr. Hunter.—L. I. SMITH. (Original manuscript received June 27, 1932.)

(2) Stanley. J. Am. *Concrete Inst.*, **49**, 349-541 (1930).

(3) Seayna, *Przemysl Chem.*, **12**, 637–47 (1928).

Ethyl Ether.—Commercial ether was washed three times with saturated potassium permanganate solution, once with water and dried successively over calcium chloride and phosphorus pentoxide. It was finally distilled from phosphorus pentoxide and kept over sodium.

Dimethylaniline.—Commercial dimethylaniline was acetylated, distilled, frozen out and finally vacuum distilled; m. p. 2.0°, b. p. 59.5–63° at 5 mm.

Trimethylamine.—A solution of pure trimethylamine hydrochloride was dropped on solid sodium hydroxide. The escaping gas was passed over soda lime, anhydrous barium oxide, metallic sodium and finally condensed with liquid air

The Preparation of Complexes not Containing Hydrocarbons

Ether–Aluminum Chloride Complex.—This complex was prepared by the method of Frankforter and Daniels[4]

Anal. Calcd. for $Al_2Cl_6{\cdot}2(C_2H_5)_2O$: Al, 13.01. Found: Al, 13.57, 13 18, 13.01, 13.00, 13.19.

Aluminum Chloride–Dimethylaniline Complex (1 : 1).—This was made by treating a quantity of aluminum chloride with a slight excess of dimethylaniline in carbon bisulfide solution. The solution turned dark green. Upon shaking, this green color disappeared and the solid aluminum chloride changed to orange or a dark red in color. When about half an equivalent of dimethylaniline had been added, a red oil, insoluble in carbon bisulfide, appeared. At the equivalent point the solution was a very dark red. Further addition of dimethylaniline caused the solution to become dark green.

When the green solution was cooled, a dark green precipitate appeared. Repeated extractions of this precipitate with boiling carbon bisulfide gave a compound which crystallized in large colorless plates. These crystals were fairly soluble in boiling carbon bisulfide but were quite insoluble in the cold. They were very hygroscopic, turned green in air and were decomposed by water to give dimethylaniline.

Anal. Calcd. for $Al_2Cl_6\ 2C_6H_5N(CH_3)_2$: Al, 10.60; N, 5.52. Found: Al, 10.53, 10.68, 10.83, 10.77, 10.51, 10 61; N, 5.44, 5.50, 5.27, 5.50, 5.30.

Aluminum Chloride Dimethylaniline (2 : 1).—The red oil mentioned above was separated from the carbon bisulfide and unchanged aluminum chloride, extracted ten times with ten times its volume of boiling carbon bisulfide (to remove 1:1 complex), and then heated for fifteen minutes at 75° under vacuum.

Anal. Calcd. for $Al_2Cl_6{\cdot}C_6H_5(CH_3)_2$: Al, 13.91; N, 3.60. Found: Al, 13.81, 13.93, 13.99, 13.96; N, 3.49, 3.35, 3.33, 3.53.

Experiments with Acetylene

At room temperature there was very little reaction between acetylene and aluminum chloride. However, at 100° adsorption and reaction were very rapid. There were no liquid products. Analysis of the darkened catalyst indicated the formation of a complex of the approximate composition $AlCl_3\ C_2H_2$. The presence of ether vapor caused an immediate darkening of the catalyst and liquid products resulted. If acetylene was bubbled through ether and then passed over aluminum chloride an extremely exothermic reaction took place and liquid products were formed which were decomposed violently by water to give hydrogen chloride and a dark brown, cuprene-like material. The aluminum content of such liquid products varied between 14.07 and 14.8%. The formula, $Al_2Cl_6\ (C_2H_5)_2O{\cdot}C_2H_2$ requires 14 7% aluminum.

Since the presence of ether vapor had such a marked effect upon the reaction, it seemed likely that the ethyl ether–aluminum chloride complex would have a similar effect. However, there was no reaction whatever between acetylene and the ether–aluminum chloride complex at room temperature or at 100°. Similarly, the aluminum

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(4) Frankforter and Daniels, THIS JOURNAL, 37, 2560 (1915).

chloride–dimethylaniline complex failed to catalyze the polymerization of acetylene at room temperature or at 100°. Trimethylamine completely stopped the adsorption of acetylene by aluminum chloride even at 100°.

Experiments with Ethylene

Ethylene was adsorbed slowly by anhydrous aluminum chloride to give a very small amount of a deep red oil. The catalyst, however, gave up most of the adsorbed gas when heated. Neither heat nor ether vapor accelerated the reaction.

There was no reaction between the ether–aluminum chloride complex or the dimethylaniline–aluminum chloride complex and ethylene, either at room temperature or 100°.

Experiments with Isobutylene

Isobutylene was extremely reactive toward aluminum chloride. Liquid products formed immediately when the hydrocarbon was allowed to come in contact with the aluminum chloride. One of the products was a colorless oil; the other a dark-red viscous oil, insoluble in the colorless product. The colorless liquid had an average molecular weight of 200 and a bromine number of 10-15. The red oil was a complex with an aluminum content averaging 11.5%, which when again treated with isobutylene yielded additional colorless liquid and the aluminum content of the complex dropped to approximately 8.75% When the treatment of the red oil with isobutylene was carried out at 140" the resulting complex contained about 10.5% aluminum. Treatment of these red viscous complexes with water yielded yellow oils with molecular weights of 260-275.

Isobutylene containing ether vapor reacted vigorously with aluminum chloride to form a red viscous oil with an aluminum content of 11.8–12.3%. The percentage of aluminum decreased to 10.3–10.45% when ether-free isobutylene was passed through this red viscous oil and further treatment even at elevated temperatures failed to alter appreciably the aluminum content of the complex.

The complex of dimethylaniline and aluminum chloride (1:1) failed to react with isobutylene at room temperature; at 140° the color of the complex changed from very pale green to a cherry red, but no layer of hydrocarbons appeared and the composition of the complex remained unchanged. When the 2:1 complex of dimethylaniline and aluminum chloride was treated with isobutylene there was immediate evidence of reaction; a colorless oily layer formed and the composition of the complex changed until it became inactive, at which point it contained 10.48% aluminum and 2.63% nitrogen. The values calculated for the complex $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2 \cdot 2C_4H_8$ are aluminum 10.8% and nitrogen 2.80%.

Discussion

In nearly every case of complex compound formation with aluminum chloride, aluminum functions with a coordination number of 4. Chlorine is not a usual donor for a coördinate bond. However, it should be able to act as such since it has three available pairs of electrons for coordination. It may do so in Al_2Cl_6. Such a coordinate bond should be easily broken giving an "unsaturated" aluminum atom which could take up two electrons from a more active donor.

A possible interpretation of the nature of the complexes formed between aluminum chloride and unsaturated aliphatic compounds is as follows: It has often been suggested that the activated olefinic bond may be represented by the following polarized structure: $)C{:}\underset{\cdot\cdot}{C}\langle$ and it is quite conceivable that a molecule of aluminum chloride could accept the "free" electron pair to give an activated complex in which one of the carbon atoms would momentarily be three covalent. Such a complex should be an excellent catalyst for polymerization, for if such an activated molecule should come in contact with another molecule of an olefin, immediate combination would result, by virtue of the highly unsaturated nature of the carbon atom containing only six electrons in its outer shell.[5] This new complex of higher hydrocarbon content would still be in an activated state, and could therefore react with another molecule of olefin in the same manner as it combined with the first. It can be seen that a long chain of carbon atoms might result from condensation of incoming olefin molecules with those already present in the complex. The length of these chains will depend on the heat of reaction, the ability of the coordinate bond to maintain this combination, and the possibility of ring formation.

A complex of aluminum chloride with an electronically saturated compound which has given a pair of electrons to aluminum (such as the ether–aluminum chloride complex) should not react with olefins and should not be a catalyst for polymerization. This has experimental support since it was found that this complex is not a catalyst for polymerization of acetylene or ethylene. However, it is a catalyst for the polymerization of isobutylene. This may be due to the fact that since oxonium compounds are not particularly stable, in certain cases an electron pair furnished by the hydrocarbon is more to be preferred by the aluminum chloride than that furnished by the oxygen of the ether. Isobutylene, which shows a greater reactivity, *per se*, than either ethylene or acetylene,[3,6] is apparently able to displace the ether in such a complex.[7] Since nitrogen in tertiary amines

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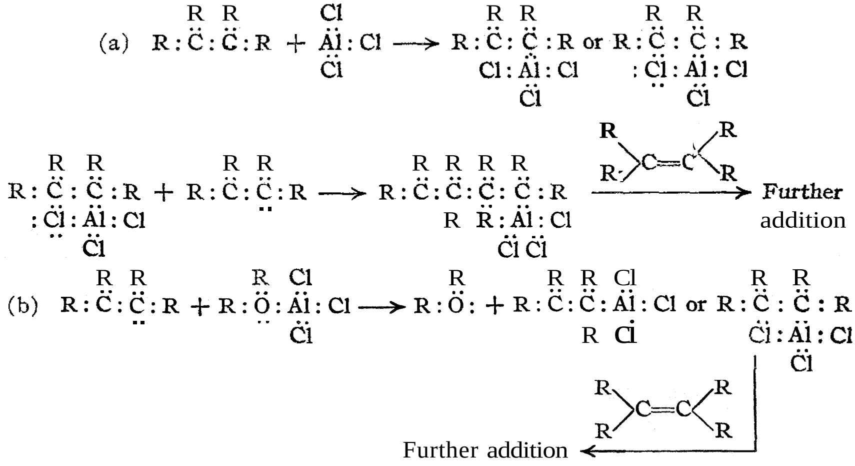
[5] Or we may accept the opinion of Dr. Sidgwick (N. V. Sidgwick, private communication,) that it contains six of its own electrons and two electrons which are donated by a chlorine atom.

[6] Lebedev. *Ber.*, **58B**, 1138 (1925).

[7] If we accept Dr. Sidgwick's picture for the olefin–aluminum chloride complex, the combination with a second molecule of olefin involves the breaking of a C–Cl coördinate link and formation of a C–C linkage. The breaking of an Al–O coördinate link and formation of an Al–C link is essentially the same sort of a transformation. The two processes may be represented electronically as follows.



has a strong tendency to coordinate with unsaturated atoms (as in the amine oxides) the 1:1 complex of aluminum chloride and dimethylaniline should be stable in the presence of olefins and should not be a catalyst for the polymerization of the latter, and this was found to be the case. More striking yet, it was found that the introduction of trimethylamine vapor during adsorption runs on acetylene, ethylene and isobutylene stopped adsorption completely. Thus it seems clear that an activated olefin molecule may cause the rupture of a C–Cl coordinate link, or even of an Al–O coordinate link, but is unable to break the much stronger Al═N link.

Summary

1. A study has been made of the reaction of aluminum chloride with acetylene, ethylene and isobutylene.
2. A study has been made of the action upon acetylene, ethylene and isobutylene of some organic complexes of aluminum chloride.
3. A theory of polymerization based on the electronic structures of aluminum chloride and olefins has been advanced.

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The Yields of Some Organolithium Compounds by the Improved Procedure

BY HENRY GILMAN, E. A. ZOELLNER AND W. M. SELBY

Introduction

The valuable and elegant studies by Ziegler and Colonius[1] have pointed the way to the convenient preparation of organolithium compounds. Latterly it was shown that many of these compounds are readily accessible by the simple procedures used for the preparation of Grignard reagents, and in yields closely approximating those noted with organomagnesium compounds.[2] Incidental to other studies, some of which are reported in the following papers, it was necessary to prepare some new organolithium compounds and to determine the limits of applicability of several typical preparations. The results are given in the Experimental Part, and in the discussion of them which follows it will be observed that some organic halides which form Grignard reagents with great ease do not form any significant quantity of organolithium compound by the simplified procedure. On the other hand, some halides which react very sluggishly with magnesium enter into prompt reaction with lithium to give excellent yields of organolithium compounds.

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(1) Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

(2) Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

Experimental Part

The general analytical procedure is that previously described. [illegible] few alterations in manipulation were introduced. First, the inverted test-tube holders for the metal are unnecessary. It is sufficient to remove the coating by scraping, and then to wash with dry ether. Second, the cutting of lithium into many fine pieces is readily effected by sharp "bandage scissors" of short blade length and long handles. These fine pieces are untarnished when the effluent inert gas (dry nitrogen) is rapid.

The results given in Table I are those obtained under three sets of conditions. In the "A-ccnditions," 0.05 mole of RX compound is used, 40 drops (or 0.3–0.4 g. of the solid) being used to start the reaction and the remainder in 15 cc. of ether is added over a period of 30–35 minutes (about 4–5 drops per five seconds). The 0.76 g. (0.11 atom) of lithium, cut into 30–32 pieces, is added to 15 cc. of ether contained in the graduated reaction flask. Accordingly, the total quantity of ether used is 30 cc. or 0.3 mole. The mixture is stirred at the outset, and heat is applied externally at the beginning and later also if the heat of reaction is insufficient to cause gentle refluxing. Stirring and refluxing are continued for one hour; the diluent (either ether or benzene) is added to bring the solution to the 100-cc. mark; and then, after a few minutes of stirring to get a homogeneous solution, the flask is detached and allowed to stand for thirty minutes, after which time samples are removed for titration.

The "B-conditions" are essentially those used to determine the drop in yield, when the halide is added at once in 15 cc. of ether to the cut lithium, heat being applied externally until the reaction starts, which is usually one-half to one minute. The "C-conditions" differ from the "A-conditions" only in the degree of fineness of the lithium, the 0.76 g. being cut into 165–170 rather than 30–32 pieces.

TABLE I

YIELDS OF SOME ORGANOLITHIUM COMPOUNDS

	Halide	% Yield under A-, B-, C-conditions A	B	C		Halide	% Yield under A-. B-, C-conditions A	B	C
1	CH_3I	73.6[a]	65.5	81.5	12	1,4,2-(CH_3)-[(C-			
2	*n*-C_4H_9Cl	76.1	67.5[b]	77.1		$H_3)_2CH]C_6H_3Br$	74.0	69.2	90.0[l]
3	*n*-C_4H_9Br	59.0[c]	42.8	68.8[d]	13	*o*-$CH_3OC_6H_4Br$	84.2	86.0	87.9
4	*n*-$C_{11}H_{12}Br$	38.5	30.2	[e]	14	*p*-$CH_3OC_6H_4Br$	75.4	66.0	87.9[m]
5	Cyclo-$C_6H_{11}Cl$	23.0	19.0[f]	24.3	15	*o*-$C_2H_5OC_6H_4Br$	73.0[n]	75.2	82.6
6	C_6H_5Cl	35.4[g]	35.0	48.7	16	*p*-$C_2H_5OC_6H_4Br$	76.7[n]	76.3	92.7
7	C_6H_5Br	95.2[h]	91.1	97.5[i]	17	*p*-$(CH_3)_2NC_6$-			
8	C_6H_5I	80.1	80.7	82.8		H_4Br	94.8[o]	95.0	96.1
9	*o*-$CH_3C_6H_4Br$	93.3	85.6	97.0[j]	18	α-$C_{10}H_7Br$	79.0[p]	82.4	96.0
10	*m*-$CH_3C_6H_4Br$	85.1	85.0	93.7[k]	19	β-$C_{10}H_7Br$	74.0	76.3	83.1
11	*p*-$CH_3C_6H_4Br$	97.6	95.6	99.2	20	*p*-$C_6H_5C_6H_4Br$	76.7[q]	73.9	81.5

[a] The yield is less with methyl iodide from unsealed containers. Freshly distilled methyl iodide, or methyl iodide from sealed containers, is recommended. Refluxing for 15 or 30 or 45 minutes gives about the same yield. A yield of 82% was obtained under A-conditions with 0.1 atom of lithium and 0.125 mole of methyl iodide. A patent by Ziegler and Colonius (German patent 512,882) mentions the preparation of methyllithium from methyl chloride or bromide, using methyl iodide as a catalyst. Undoubtedly the A-conditions with 10–12 molecular equivalents of ether will give yields as high as those described in the C-conditions with fine lithium. It is significant that methyllithium is stable for weeks in ether [Ziegler and Zeiser, **Ann.**, **485**, 174 (1931)].

[b] The "drop yields" are inclined here to be erratic, and the 67.5% is a minimum yield.

[c] The yield is markedly decreased without stirring, dropping in some cases to **10.5%.**

[d] The finely cut lithium in the n-butyl bromide and methyl iodide experiments tends to aggregate into a single mass. However, when this does happen it is apparently without any significant effect on the yield.

[e] No experiment was made with very fine lithium. *n*-Laurylmagnesium bromide is obtainable in yields of 85.3%, and the decrease on rapid addition of lauryl bromide to magnesium is 11%. The average drop in yields of Grignard reagents on rapid addition of RBr compounds from n-butyl to n-octyl is about 15%.

[f] A reaction takes place with cyclohexyl bromide, but no appreciable quantity of organolithium compound was formed.

[g] Occasional erratic yields with chlorobenzene may be due to varying coatings with lithium chloride. Orienting experiments with a mixture of chlorobenzene and bromobenzene indicate that the yield of phenyl-lithium is higher than that realized from the sum of the yields when these halides are used separately. Because phenylmagnesium chloride can be obtained in excellent yields without the use of a solvent [THIS JOURNAL, 52,3330 (1930)] it is possible that corresponding conditions may be useful in the reaction between chlorobenzene and lithium.

To reduce the coating effect of lithium chloride, the lithium was added in three separate portions with refluxing for one hour after each addition. The yield was **51.2%.**

The yield was 52% when a steel stirrer with knife edge was used to remove the coating partially; and with **310** pieces of lithium and refluxing for one and one-quarter hours, the yield was **53.5%** and the solution was light yellow in color.

[h] The yield is **96.2%** when the halide is added over one hour rather than thirty minutes. However, with ten instead of six equivalents of ether the yield is 98.5%, and this is due in part to the lesser precipitation of lithium bromide. Under these conditions, the yield being practically quantitative, there is no improvement when the halide is added more slowly. No experiments with intermediate quantities of ether were tried, and quantitative yields may possibly be obtained with a ratio of ether between six and ten equivalents. When more than six equivalents of ether are used it is recommended that three be used to dilute the halide and the rest be added initially to the lithium.

With the fine pieces of lithium used under these conditions there is no drop in yield when the bromobenzene is added at one time.

[i] Addition of o-bromotoluene at one time, under these conditions, gives a 95% yield. The already high yield was not increased with ten equivalents of ether.

[k] Spontaneous refluxing ceased after twenty minutes, and at the same time the solution started to deposit lithium bromide. As in other related cases, external heat was then applied so that gentle refluxing was maintained throughout the preparation.

The yields under C-conditions are erratic at times. In the present case one yield of 88% was noted. The difficulty may be due to the varying agglomeration of the finely cut lithium. Check results within **2%** are obtainable with the **A**- and B-conditions.

With ten molecular equivalents of ether, instead of six, under A-conditions, the yield is 98.8%.

The very fine lithium is unnecessary for high yields, because 10–12 equivalents of ether in the A-conditions also gave a 90% yield.

[m] This experiment emphasizes in a striking manner the desirability of continuous refluxing throughout the preparation. If external heat is applied after the spontaneous heat of reaction has subsided, the yield is significantly decreased even though the time interval is brief. This may be due to a partial deposition of lithium halide which is subsequently removed with difficulty.

Here, also, fine lithium is unnecessary, for the yield under A-conditions with **12** equivalents of ether is 93%, and with **14** equivalents somewhat less.

[n] The effect of more ether was not studied, but **it** is probable that **10–12** equivalents

of ether will give yields in excess of 90%. This applies also to α- and β-bromonaphthalenes and p-brornodiphenyl.

[o] The high yield of *p*-dimethylaminophenyl-lithium irrespective of the rate of addition of halide or the fineness of the lithium suggested extra confirmation. With the assistance of Mr. E. B. Towne, the unused lithium was carefully assembled and shown to correspond with the high titration values. Also, derivatives like the furan analog of malachite green by Mr. R. H. Kirby, were prepared.

The recent description of this preparation by Austin [THIS JOURNAL, 54, **3726** (1932)] directs attention to the difficulty of titration because of the colored solutions By titrating directly in the presence of phenolphthalein he noted that the change from red to preen could be observed quite satisfactorily. The present results were completed before the appearance of that paper. Subsequent to showing that neither dimethylaniline nor *p*-bromodimethylaniline was separately responsible for the blue color (and that neither one interfered essentially with the titration values), some observations revealed that the difficulty in titration was due to the action of air on *p*-dimethylaminophenyl-lithium. Accordingly, the titrations were subsequently carried out in a nitrogen atmosphere and the distilled water used was boiled to expel dissolved gases. When the air is excluded, the faint reddish tint at neutrality is not a source of inconvenience inasmuch as the subsequent addition of **2–3** drops of base gives the solution a pronounced red color. Methyl orange is apparently unsatisfactory as an indicator. Carbonation of an aliquot by Mr. P. R. Van Ess gave crystal violet, but the troublesome bluish color is not due exclusively to carbon dioxide.

[p] On standing for a moderate time there was no separation in the ether solution as is frequently observed with α-naphthylmagnesium bromide. The organolithium compound in an ether–benzene solution has an opaque purple color [see Vesely and Stursa, *Coll. Czechoslov. Chem. Comm.*, *4*, **139** (1932)].

[q] Reaction set in at once, and this is in sharp contrast with the start of reaction between p-bromodiphenyl and magnesium in ether. A slightly larger than usual quantity of ether was used. The solution of organolithium compound is dark blue in color.

Discussion of Results

Although the organolithium compounds were prepared under conditions closely resembling those for the synthesis of the related Grignard reagents, it is obvious that there are some marked differences between the two classes of organometallic compounds. Some RX compounds undergo more ready reaction with lithium than with magnesium. This is particularly true with compounds like chlorobenzene, *p*-chlorotoluene (which gave a 63% yield), α-chloronaphthalene,[3] *p*-bromodiphenyl and *p*-bromodimethylaniline.[4] On the other hand, some compounds which undergo ready reaction with magnesium in ether appear, under corresponding conditions, to be essentially unaffected by lithium. This is particularly true of some polyhalogen aryl types like *p*-chlorobromobenzene and P-dibromobenzene. *p*-Bromoiodobenzene does react to give an organolithium compound, but in some orienting experiments p-diiodobenzene appears to be without reaction. Fortunately, these cases admirably supplement each other and so make more readily available a larger variety of reactive organometallic compounds. There are at this time insufficient

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(3) Vesely and Stursa, *Coll. Czechoslov. Chem. Comm.*. *4*, *139* (1932).

(4) Austin, THIS JOURNAL, **54**, 3726 (1932).

data to warrant predictions as to the types of RX compounds with relatively inert halogen which will enter into reaction. This difficulty is increased by the erratic behavior of some halides in their reaction with lithium. An illustration is the reaction with β-bromonaphthalene. The β-naphthyl-lithium was not obtained recently[3] in any quantity, whereas under optimal conditions we have prepared it in excellent yields. The difficulties are not due solely to impure halides, although it is quite true that impure halides markedly affect both the starting of reaction and the yield of organolithium compound, and to an extent greater than that observed with Grignard reagents.

The general limits of usefulness of RX compounds have been defined by Ziegler and co-workers. However, methyl iodide is at least one exception to the rule that alkyl iodides are useless. Incidentally methyl iodide, as might have been predicted on the basis of anomalous behavior of first members of homologous series, behaves unlike other alkyl iodides in its reaction with magnesium. The chief difficulty in the way of using RX compounds with active halogens is the Wurtz reaction[1]

$$\mathrm{RLi} + \mathrm{RI} \longrightarrow \mathrm{R{\cdot}R} + \mathrm{LiI}$$

This reaction explains satisfactorily why alkyl chlorides are more suitable than alkyl bromides, and why alkyl iodides, in general, are of little value. A second difficulty in the way of preparing alkyl-lithium compounds in ether is their high reactivity in splitting ethers. The aryl-lithium compounds, in agreement with their lesser activity, cleave ethers to a decidedly lesser extent. Accordingly, although ether solutions of aryl-lithium compounds can be kept for some time, the alkyl-lithium compounds in ether must be used, in general, within a few hours. Fortunately, the alkyl-lithium compounds are not only quite stable in benzene, but are obtainable in better yields in this medium.[1,2] Although alkyl- and arylmagnesium *fluorides* can be prepared, it is obvious that the reaction between fluorides and lithium should take place more readily, even though it be a relatively slow reaction.

The Wurtz reaction mentioned above is hardly peculiar to alkyl halides, because the anomalous reaction[3] between lithium and β-bromonaphthalene gave di-β-naphthyl as the sole reaction product.

With continuous refluxing, applied externally if necessary, throughout a preparation, a moderate or slow rate of addition of halide generally improves the yield, but as a rule the increase in yield is not noteworthy. A greater ratio of ether than that used in most Grignard preparations distinctly improves the yield of many organolithium compounds. The yield is also improved with the increased fineness of the lithium. This does not necessarily mean that a like high yield would be realized over a longer time with coarser lithium, because the secondary Wurtz reaction may come into play to an increasing extent to use up both RLi and RX compounds. With very fine lithium, it appears that the rate of addition of halide is inconsequential. Although lithium can be conveniently cut into many small pieces for small quantitative experiments, it is probable that the next significant advance in making organolithium compounds more accessible will come with a convenient procedure for the preparation of lithium dust or granules, possibly after the method now used for the preparation of fine sodium. A technique of this kind has already been used for some organolithium compounds,[5] the molten metal being shaken under paraffin. To conserve lithium, the paraffin wax should be treated first with sodium, by dispersing it in the wax at temperatures above the melting point of lithium, and then separate the wax, refined in this manner, from the sodium, the molten globules of which should remain clear and untarnished.[6] The advantages of finely divided metal are not due exclusively to more rapid reaction per se, but also to a relative decrease of the coating effect of lithium halides.

On the basis of observations with Grignard reagents, it is probable that larger-sized runs will, in general, give improved yields and also reduce the relative quantity of ether.

In general, as with Grignard reagents, chlorides are more suitable than bromides, and iodides are least satisfactory. With aryl-lithium compounds, bromides are generally recommended. As yet no tertiary-organolithium compound (other than triphenylmethyl-lithium types) has been prepared. No alkali metal derivatives of vinyl or substituted vinyl radicals are known? Our 34% yield by acid titration of organolithium compound from β-bromostyrene ($C_6H_5CH{=}CHBr$) is probably not an exception to this rule, because the product of carbonation is not cinnamic acid. The as yet unidentified acid may be due to the addition of lithium to a coupling product like 1,4-diphenylbutadiene-1,3. In this connection we are of the opinion that the chief mechanism of formation of organo-lithium, like other organometallic compounds,[8] is one involving free radicals.

The yield of alkyl-lithium compounds prepared in ether, decreases with the length of the chain. This decrease in yield, however, is greater than might have been predicted in view of the relatively high yields of *n*-laurylmagnesium bromide.

The authors are grateful to Mr. R. H. Kirby for assistance.

Summary

Yields have been determined of some organolithium compounds prepared in ether after the general procedure for the preparation of Grignard reagents. Optimal conditions and general limitations are discussed.

AMES, *IOWA*

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(5) Ziegler, German patent 512,882.

(6) H. P. A. Groll, private communication; THIS JOURNAL, 52, 2998 (1930).

(7) Wooster, *Chem. Reviews*, 11, [1] 21 (1932).

(8) Gilman and Brown, *Rec. trav. chim.*, 50, 184 *(1931).*

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Ketones by the Carbonation of Organolithium Compounds

BY HENRY GILMAN AND PAUL R. VAN ESS

Introduction

Carbonation is one of the best methods for the characterization of reactive organometallic compounds because the acid formed by this reaction is, in general, readily isolated, purified and identified. However, the carbonation of phenyl-lithium has been reported to give only traces of benzoic acid,[1] and it has been stated that low yields of acid are observed in the carbonation of many Grignard reagents. Actually, the yields of acids from RMgX compounds, when carbonation is effected under optimal conditions,[2a] are excellent and in many cases approach theoretical values based on available Grignard reagent.[3] A low yield of benzoic acid from phenyl-lithium has been confirmed, and we have found that the poor yield is due to an uncommonly high yield (upward of 70%) of benzophenone. The carbonation of other organolithium compounds indicates that the reaction may be of value as a means of synthesizing some ketones.

Fortunately, it is possible to obtain good yields of acids by carbonating organolithium compounds under special conditions. An essential factor is a high local concentration of carbon dioxide, and this can be realized by procedures already described for the carbonation of Grignard reagents: namely, the addition of organometallic compound to solid carbon dioxide[4] or spraying the organometallic compound into an atmosphere of carbon dioxide.[2a,c]

Mechanism of Carbonations.—It is generally agreed that the following are the chief reactions involved in the carbonation of an RMgX compound.

$$\text{(I)}\quad \mathrm{RMgX} + \mathrm{CO_2} \longrightarrow \mathrm{RCOOMgX}$$
$$\text{(II)}\quad \mathrm{RCO_2MgX} + \mathrm{RMgX} \longrightarrow \mathrm{RCOR}$$
$$\text{(III)}\quad \mathrm{RCOR} + \mathrm{RMgX} \longrightarrow \mathrm{R_3COH}$$

At elevated temperatures and with a low concentration of carbon dioxide, the yield of acid is depressed and relatively large quantities of ketone and tertiary alcohol can be obtained.[4a,2b] Obviously, steric influences can operate to give high yields of acid (or/and ketone) where tertiary alcohol is a preponderant product in the absence of steric hindrance.

With aryl-lithium compounds, when carbon dioxide is bubbled into or

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(1) Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

(2) (a) Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924); (b) Gilman and St. John, *Rec. trav. chim.*, **49**, 1172 (1930); (c) Gilman and Harris, *ibid.*, **50**, 1052 (1931); (d) Gilman and Zoellner, THIS JOURNAL, **53**, 1945 (1931).

(3) The hitherto exceptional cases, allyl- and β-styrylmagnesium bromides, have since been found to give satisfactory yields of acids.

(4) (a) Bodroux, *Bull. soc. chim.*, 31, 24 (1904); (b) Spencer and Stokes, J. Chem. *Soc.*, **93**, 70 (1908).

over the surface of the solution, the chief product is a ketone and practically no tertiary alcohol is formed. This indicates that the salt, RCOOLi, is converted to a di-lithium salt of a dihydroxymethane and not to the ketone.

(IV) 

$$\text{RCOOLi} + \text{RLi} \longrightarrow \text{R—}\underset{\text{OLi}\ \ \text{OLi}}{\text{C}}\text{—R}$$

$$\text{(V)}\quad \text{RCOR} + \text{RLi} \longrightarrow \text{R}_3\text{COH}$$

Were the ketone formed as an intermediate, it is reasonable to suppose that it would react at once with the excess of RLi compound to give a tertiary alcohol. Benzophenone, for example, reacts (V) immediately and practically quantitatively with phenyl-lithium to give triphenylcarbinol.[1,5a]

A di-magnesium salt or its equivalent (like ) may or may not be an intermediate in the carbonation of organomagnesium compounds, depending somewhat on the relative reactivity of the particular Grignard reagent. Organolithium compounds are distinctly more reactive than organomagnesium compounds[5b,6] and this would reflect itself in a tendency to add simultaneously or consecutively to the two carbonyl linkages in carbon dioxide to give the di-lithium salt. With RMgX compounds the —O metal linkage might be removed in accordance with Reaction (II) prior to addition of another molecule of RMgX to the available carbonyl group in the salt. Or the di-magnesium salt may lose magnesium oxide or its equivalent, more readily than the corresponding di-lithium salt loses lithium oxide, to give the ketone.

If Reaction (IV) is valid it might be expected that lithium benzoate would react with phenyl-lithium to give a satisfactory yield of benzophenone. This finds support in the formation of benzophenone in a 70% yield to the apparent exclusion of triphenylcarbinol. The reaction may find some application in the preparation of mixed ketones inasmuch as lithium *n*-butyrate and phenyl-lithium give a 62% yield of *n*-butyrophenone, $C_6H_5COCH_2CH_2CH_3$.

It is reasonable to conclude that if the reaction of a salt with an organolithium compound is arrested at the ketone stage because of the firmness of attachment of the metal to oxygen, then rubidium or cesium salts might be expected to give yields of ketone sufficiently high to commend the method as one of choice for the synthesis of mixed ketones, many of which are now relatively inaccessible.

(5) (a) Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932); (b) Gilman and Kirby, *ibid.*, **55**, 1265 (1933).

(6) Incidentally, it was shown that phenyl-lithium is carbonated more rapidly, at about 0°, than phenylmagnesium bromide. These experiments were carried out quantitatively using a flowmeter and the color test for reactive organometallic compounds. The yield of benzoic acid from the phenylmagnesium bromide experiments was 85%.

Experimental Part

Carbonation of **Organolithium** Compounds.--Carbonation of phenyl-lithium under ordinary conditions used with Grignard reagents,[2a] gave 4% benzoic acid, 70% benzophenone and no triphenylcarbinol. In the spray-method,*' when phenyl-lithium in ether was added dropwise slowly, the yield of benzoic acid was 37% and the yield of triphenylcarbinol was 8.7%. However, when phenyl-lithium was added in jets of such size and so spaced that the temperature was maintained at 0°, the corresponding yields were 47.5 and 8.1%, respectively. The jet-wise addition of phenyl-lithium to solid carbon dioxide gave 60% of benzoic acid, 15.4% of benzophenone and no triphenylcarbinol. Under corresponding conditions, phenylmagnesium bromide gave a 90% yield of benzoic acid. The carbonation of phenyl-lithium at the boiling point of ether gave 1.6% of benzoic acid, 76% of benzophenone and no significant quantity of triphenylcarbinol.

Carbonation of *p*-tolyl-lithium, starting at 0° and ending at 15°, gave 1% of *p*-toluic acid and 77–81% of di-*p*-tolyl ketone. Under corresponding conditions, *o*-tolyl-lithium gave 35% of o-toluic acid. This relatively higher yield of acid is probably due to steric influences

The yield of di-n-butyl ketone obtained by carbonating an ether solution of n-butyl-lithium cooled by an ice–salt bath was 45–50%. The ketone was characterized by its semicarbazone. Carbonation of 0.09 mole of n-butyl-lithium in benzene at room temperature gave 13% of the ketone and 0.9 g. of a liquid distilling at 102–105° (6 mm.). This probably is tri-n-butylcarbinol, and its formation reflects the greater reactivity of n-butyl- over phenyl-lithium.

Lithium Salts and Organolithium Compounds.—A suspension of 0.136 mole of lithium benzoate in ether was refluxed for five and one-half hours (to disappearance of color test) with 0.1 mole of phenyl-lithium. The yield of benzophenone was 70% and no triphenylcarbinol was isolated. With an ether–benzene medium, the time was ten hours and the yield of ketone 68%.

After refluxing lithium butyrate and phenyl-lithium in ether for eight hours, a 62% yield of n-butyrophenone was obtained. It was characterized by its semicarbazone.

In an orienting experiment, 0.1 mole of n-butyl-lithium, prepared from n-butyl chloride in benzene in a 55% yield, was refluxed with lithium *n*-butyrate (with benzene alone as the medium) for twenty-four hours to give a 10% yield of n-propyl n-butyl ketone. Apparently, ether is a better medium for such reactions.

Benzoyl Chloride and Phenyl-lithium.—Inasmuch as the reaction $C_6H_5COCl + C_6H_5MgI \longrightarrow (C_6H_5)_2C{=}O$ gives benzophenone in a 68.5% yield,[7] when the Grignard reagent is added to the acid chloride, it was of interest to learn whether a corresponding reaction with phenyl-lithium would give satisfactory yields of benzophenone. Actually, no benzophenone was obtained and the yield of triphenylcarbinol was 42%. The reverse mode of addition (benzoyl chloride to phenylmagnesium bromide) gives a 92% yield of triphenylcarbinol.[2b] It is probable that a study of optimal conditions like slow addition, marked cooling and high concentrations of benzoyl chloride will give ketones with organolithium compounds, but the method appears of little promise for the synthesis of ketones.

Miscellaneous.—The addition of 0.051 mole of benzoic acid to 0.102 mole of phenyl-lithium in ether gave 37.2% of benzophenone and 14.1% of triphenylcarbinol. The formation of triphenylcarbinol in this reaction is somewhat anomalous, because a reaction of lithium benzoate and phenyl-lithium gave 70% of ketone and no carbinol. One explanation for the formation of carbinol turns on the possible dehydration of benzoic acid

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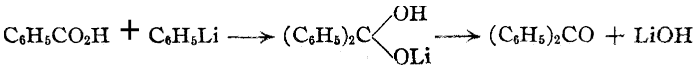
(7) Gilman and Mayhue, *Rec. trav chim.*, **51**, 47 (1932).

by phenyl-lithium to give benzoic anhydride, which in turn should react with phenyl-lithium to give some "free" benzophenone, and this would react at once with phenyl-lithium to give triphenylcarbinol.

$$\begin{gathered} 2C_6H_5COOH + 2C_6H_5Li \longrightarrow (C_6H_5CO)_2O \\ (C_6H_5CO)_2O + C_6H_5Li \longrightarrow C_6H_5CO_2Li + (C_6H_5)_2C{=}O \\ (C_6H_5)_2C{=}O + C_6H_5Li \longrightarrow (C_6H_5)_3COH \end{gathered}$$

It has been suggested that the following competing reactions are equally reasonable to account for the formation of triphenylcarbinol.

$$C_6H_5CO_2H + C_6H_5Li \longrightarrow C_6H_5CO_2Li + C_6H_6$$



$$C_6H_5CO_2H + C_6H_5Li \longrightarrow (C_6H_5)_2C\begin{cases} OH \\ OLi \end{cases} \longrightarrow (C_6H_5)_2CO + LiOH$$

In the latter (addition) reaction, the monolithium derivative would lose lithium hydroxide to form benzophenone which in turn would give triphenylcarbinol,

Finally, in order to determine whether organolithium compounds can be prepared without impairment of yield in the absence of an inert atmosphere,[5a] phenyl-lithium was prepared both under the usual conditions for the Grignard reagent and in an inert atmosphere. Each solution was treated with benzophenone and the yield of triphenylcarbinol from the phenyl-lithium prepared in an inert atmosphere was slightly higher than that obtained with no inert atmosphere. Accordingly, it is recommended that organolithium compounds be prepared in an atmosphere of nitrogen or hydrogen. Of course, closed containers are unnecessary."'

Summary

Usual procedures for the carbonation of organolithium compounds give high yields of ketone and very little acid. The formation of acids for the characterization of organometallic compounds is markedly improved by the use of solid carbon dioxide or by the gas in the spray-procedure. A second method for the preparation of ketones, both simple and mixed, in satisfactory yields from organolithium compounds involves interaction with salts. A mechanism of carbonation is considered.

AMES, IOWA

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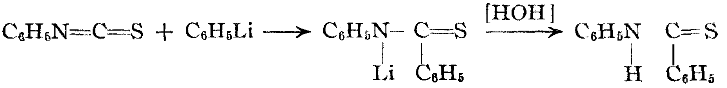
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Mechanism of Reaction of Phenyl-Sodium and Phenyl-Lithium with Phenyl Isothiocyanate

BY HENRY GILMAN AND FRITZ BREUER[1]

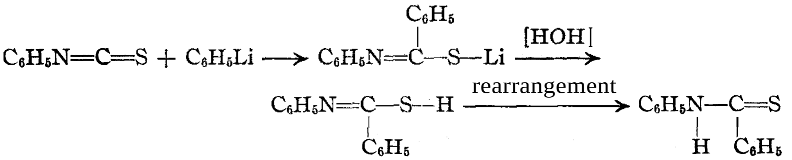
Introduction

Phenyl isothiocyanate has been employed rather extensively in reactions for the characterization of organo-alkali compounds, and the following mechanism is typical of those postulated for such transformations.



$$C_6H_5N{=}C{=}S + C_6H_5Li \longrightarrow \underset{Li}{C_6H_5N}-\underset{C_6H_5}{C}{=}S \xrightarrow{[HOH]} \underset{H}{C_6H_5N}-\underset{C_6H_5}{C}{=}S \qquad (I)$$

There is no doubt concerning the formation of thiobenzanilide (or other thio-anilides) as the main product of this reaction. The product, however, throws no light on the mechanism of reaction; and the organo-alkali compound might have added to the thiocarbonyl rather than to the anil linkage, as follows



$$C_6H_5N{=}C{=}S + C_6H_5Li \longrightarrow C_6H_5N{=}\overset{C_6H_5}{C}-S-Li \xrightarrow{[HOH]}$$
$$C_6H_5N{=}\underset{C_6H_5}{C}-S-H \xrightarrow{\text{rearrangement}} \underset{H}{C_6H_5N}-\underset{C_6H_5}{C}{=}S \qquad (II)$$

The latter mechanism has been established definitely with Grignard reagents,[2a] and from other studies[2b] it appears that RMgX compounds add to the terminal unsaturated linkage in compounds like ketenes, isocyanates and thionylamines which have terminal cumulated unsaturated linkages. By analogy, it would appear that the mechanism postulated (I) for organo-alkali compounds is incorrect, and that such compounds would react like Grignard reagents in accordance with Reactions (II). However, it is now known that there are occasional differences in the course of reaction of a selected reactant with an organo-alkali and the corresponding organomagnesium compound.[3]

The mechanism of reaction has been established by treating the reaction mixture, prior to hydrolysis, with dimethyl sulfate in order to identify the nature of the metallic combination prior to any rearrangement of an enolic form which might arise on hydrolysis. With Reactions (I), replacement of lithium on nitrogen by a methyl group should give N-methyl-thiobenzanilide; and, with Reactions (II), replacement of lithium on sulfur by a methyl group should give S-methylthiobenzanilide, as follows

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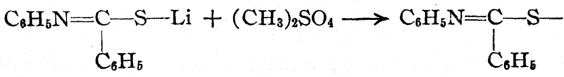
[1] Austro-American Exchange Fellow.

[2] (a) Gilman and Kinney, THIS JOURNAL, 46, 493 (1924); (b) Gilman, Kirby and Kinney, *ibid.*, 51, 2252 (1929).

[3] See the following paper, p. 1265.

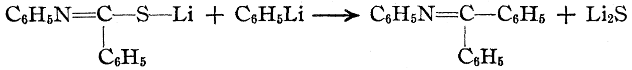


$$C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}S{-}Li + (CH_3)_2SO_4 \longrightarrow C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}S{-}CH_3$$

(III)

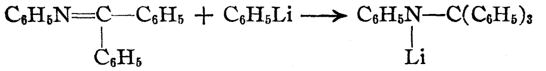
Actually, the S-methyl-thiobenzanilide (III) was isolated with both phenyllithium and phenyl-sodium, and the oily residues on hydrolysis yielded no N-methylaniline—a product which should have resulted if addition took place at the anil linkage (I). Accordingly, the previously postulated mechanism is incorrect; addition occurs at the terminal thiocarbonyl group; and one may more confidently conclude that other terminal cumulated unsaturated compounds like ketenes, isocyanates and thionylamines undergo addition with organo-alkali compounds at the terminal unsaturated linkage, after the kind of reaction shown by Grignard reagents.

It would be reasonable to predict that a sufficient quantity of the most active organo-alkali compounds (those of cesium and rubidium) would add to both unsaturated linkages in compounds like isothiocyanates. The somewhat less active organosodium and organolithium compounds undergo apparently a reaction further than that indicated in (II) to give triphenylcarbinol and triphenylmethane. These products were not isolated in the smoother reaction with phenylmagnesium bromide, and they may arise as a consequence of the following transformations



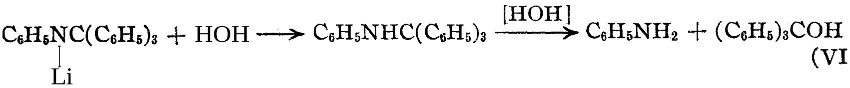
$$C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}S{-}Li + C_6H_5Li \longrightarrow C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}C_6H_5 + Li_2S$$

(IV)



$$C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}C_6H_5 + C_6H_5Li \longrightarrow C_6H_5\underset{\underset{\displaystyle Li}{|}}{N}{-}C(C_6H_5)_3$$

(V)



$$C_6H_5\underset{\underset{\displaystyle Li}{|}}{N}C(C_6H_5)_3 + HOH \longrightarrow C_6H_5NHC(C_6H_5)_3 \xrightarrow{[HOH]} C_6H_5NH_2 + (C_6H_5)_3COH$$

(VI)

Reaction (IV) does take place under forced conditions with phenylmagnesium bromide,[2b] and milder conditions may be adequate with the more reactive organo-alkali compounds. Reaction (V) occurs with phenyllithium and probably not with phenylmagnesium bromide.[3] Triphenylmethylaniline (IV) is known to hydrolyze to aniline and triphenylcarbinol, and triphenylcarbinol is convertible to triphenylmethane.

An objection to the sequence of reactions (IV ⟶ V ⟶ VI) is the absence of methylaniline which might have been expected when the reaction mixture is treated with dimethyl sulfate prior to hydrolysis. Two explanations suggest themselves. Either the steric hindrance associated with the accumulation of a maximum number of phenyl groups effectually blocked reaction with dimethyl sulfate, or dimethyl sulfate might have reacted anomalously. The only abnormal reactions now known have been observed with some furan-Grignard reagents where dimethyl sulfate replaces an –MgX group by hydrogen.

Experimental Part

Phenyl Isothiocyanate and **Phenyl-lithium.**—From 6.75 g. (0.05 mole) of phenyl isothiocyanate, 0.07 mole of phenyl-lithium and 0.09 mole of dimethyl sulfate there was obtained 3.29 g. or a 30% yield of S-methyl-thiobenzanilide which was identified by the method of mixed melting points. Hydrolysis of the oil yielded aniline, and this was characterized by the preparation of acetanilide. In another experiment, wherein the hydrolysate was allowed to stand for a longer time, there was isolated some triphenylcarbinol in addition to a 13% yield of S-methyl-thiobenzanilide. Here also the oils gave aniline, but no methylaniline, on hydrolysis. Undoubtedly, the greater quantity of oil observed in the reaction products from both phenyl-lithium and phenyl-sodium is due not only to secondary reactions growing out of the greater reactivities of organo-alkali compounds when compared with the related Grignard reagents, but also to some polymerization of the phenyl isothiocyanate. Unlike the corresponding reaction with phenylmagnesium bromide, the oily reaction product is relatively intractable and a more laborious procedure for resolution into solids is necessary.

Phenyl Isothiocyanate and Phenyl-sodium.—In this reaction, unlike that with phenyl-lithium, all reactions were carried out in anhydrous, air-free benzene. Ether cannot be used conveniently as a medium because it is readily cleaved by phenyl-sodium. The phenyl-sodium suspension (0.1 mole in 200 cc. of benzene) was added in three portions to 0.15 mole of phenyl isothiocyanate. Reaction was slow, as indicated by the color test, and the mixture was stirred and refluxed for several hours. It was then allowed to stand overnight under the nitrogen atmosphere used throughout.

Prior to the addition of dimethyl sulfate, an aliquot was removed and on hydrolysis it yielded the expected thiobenzanilide. The same product was obtained in a reaction between phenyl-lithium and phenyl isothiocyanate.

The original reaction mixture (containing a green flocculent precipitate in a clear, brown solution) was treated with 0.12 mole of dimethyl sulfate in 15 cc. of benzene. Part of the precipitate dissolved, and after refluxing for seven hours the solution assumed a reddish color. Subsequent to hydrolysis, the highly complex mixture was carefully worked up by combination processes of extraction with solvents, crystallization and distillation. The products identified were S-methyl-thiobenzanilide (a 27% yield based on phenyl isothiocyanate) and thiobenzanilide.

In a second experiment, carried out at a lower temperature (about +5°) an aliquot again gave some thiobenzanilide. Then, because a color test showed unused organometallic compound, after adding the dimethyl sulfate, the mixture was refluxed for thirty minutes. As indicative of the slow reaction due to poor contact of the reactants, it should be stated that an aliquot prior to the addition of dimethyl sulfate yielded some phenyl isothiocyanate. The products isolated were triphenylmethane, triphenylcarbinol (by crystallographic examination under the microscope), and sulfur.

Summary

Phenyl-lithium and phenyl-sodium react with phenyl isothiocyanate to give thiobenzanilide as a consequence of addition to the thiocarbonyl group, and not to the anil linkage as has been hitherto postulated in this widely used reaction for the characterization of organo-alkali compounds. The reaction is more complicated than that observed with phenylmagnesium halides, but the essential mechanisms are alike.

AMES, IOWA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Relative Reactivities of Organolithium and Organomagnesium Compounds

BY HENRY GILMAN AND R. H. KIRBY

Introduction

The color test for reactive organometallic compounds provides a means for measuring the relative reactivities of such compounds. It has been used for determining the reaction rates of various Grignard reagents with selected reactants[1a,b,c] and for distinguishing between RMgX and R_2Mg compounds.[1d] The present work, a continuation of studies on the relative reactivities of organometallic compounds, compares n-butyl- and phenyl-lithium with n-butyl- and phenylmagnesium bromides. On the basis of a series of typical reactants, there is no doubt concerning the greater reaction velocities of organolithium compounds. It has been shown recently that organolithium compounds react more rapidly than RMgX compounds with secondary amines.[2] Where comparisons can be made from the present results it is generally true that n-butyl-lithium undergoes more ready reaction than phenyl-lithium. This also is in agreement with observations like the more rapid addition of n-butyl-lithium, when compared with phenyl-lithium, to 1,1-diphenylethylene.[3] It would be ill-advised, in view of related studies with organomagnesium halides, to make sweeping generalizations to the effect that all organolithium compounds are more reactive than the corresponding Grignard reagents, and that all alkyl-lithium compounds react more rapidly than aryl-lithium compounds.

It may be held that it is unwarranted to draw conclusions on the relative reactivities of organolithium and organomagnesium compounds when the types studied are different. Thai. is, a comparison of phenyl-lithium with diphenylmagnesium might properly be considered more fair than a comparison of phenyl-lithium with phenylmagnesium bromide. However, the present available evidence shows that RMgX compounds react more rapidly than the corresponding R_2Mg compounds.[1d,e] It now appears generally true that the following is the order of decreasing activity of some highly active organometallic compounds: Cs, Rb, K, Na, Li, Mg.

Compounds which React with Organolithium but Not with Organomagnesium Types.—There are occasional functional groups which undergo reaction with organolithium compounds but not with the Grignard reagent. The outstanding illustration is the olefinic linkage in some hydrocarbons. It has been rather thoroughly demonstrated that the Grignard

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[1] (a) Gilman and Pickens, Tars JOURNAL, 47. 2406 (1925); (b) Gilman, Heck and St. John, *Rec. trav. chim.*, 49,212 (1930); (c) Gilman and St. John, *ibid.*, 49,222 (1930); (d) Gilman and Brown, Tars JOURNAL, 52, 1181 (1930); (e) Bachmann, *ibid.*, 52, 4412 (1930).

[2] Ziegler and Ohlinger, *Ann.*, 495, 84 (1932).

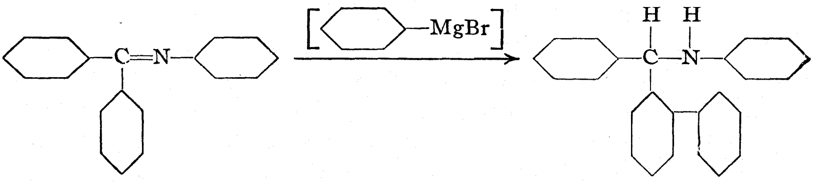
[3] Ziegler and Colonius. *ibid.*, 479, 135 (1930).

reagent does not add, in the numerous cases so far investigated, to a simple olefinic linkage. Admittedly, the apparent absence of reaction may merely be a limiting case of an extremely slow reaction.

Actually, the only important functional groups or linkages which do not undergo reaction with RMgX compounds are the olefinic and acetylenic (disubstituted) linkages. Practically all other functional groups enter into reaction with Grignard reagents. However, occasional members of a given series appear not to react with organomagnesium halides. The present striking illustrations are nitriles. p-Dimethylaminobenzonitrile has been recovered unchanged after attempted reaction with ethylmagnesium iodide and phenylmagnesium bromide;[4] and *p*-methoxybenzonitrile was observed not to undergo reaction with Grignard reagents under conditions that induced reaction with benzonitrile.[5] We have shown that each of these ketones reacts quite promptly with both methyl- and phenyl-lithium to give the normal and expected ketonic products.

Different Types of Reaction of Organolithium and Organomagnesium Compounds with a Selected Reactant.—Partly because of the different reactivities of organolithium and organomagnesium compounds it might be expected that some compounds, especially those with poly-functional groups, will undergo distinctive and different reactions with corresponding members of these organometallic types. Reactions of this kind have been observed, and are now reported, with benzophenone-anil [$(C_6H_5)_2C{=}NC_6H_5$].

Benzophenone-anil reacts decidedly slowly, if at all, when refluxed with phenylmagnesium bromide in ether.[6] However, when the ether is largely replaced by toluene and the mixture refluxed for ten hours at 90–105°, a highly unusual reaction takes place leading to the formation of *o*-phenylbenzohydrylaniline.



(I)

This secondary amine owes its formation to the unique 1,4-addition to a conjugated system which is partly lateral and partly nuclear. Apparently, the forced conditions of reaction are necessary to overcome steric hindrance inasmuch as benzal-aniline  undergoes addition with phenylmagnesium bromide to the anil linkage to give benzohydrylaniline.

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(4) Sachs and Sachs, *Ber.*, **37**, 3089 (1904).

(5) Angeli, *Atti. accad. Lincei*, [6] 3, 450 (1926) [*Chem. Abstracts*, **20**, *2843* (1926)]. See also Angeli, "Sammlung chemischer und chemisch-technischer Vorträge," 28–29, 30 (1924–27).

(6) Gilman, Kirby and Kinney, THIS JOURNAL, 61, 2252 (1929).

A similar reaction involving 1,4-addition to a nuclear-lateral conjugated system has been observed with highly phenylated ketones.[7]

Phenyl-lithium does react with benzophenone-anil in ether and the product obtained is triphenylmethylaniline.

$$(C_6H_5)_2C{=}NC_6H_5 + C_6H_5Li \longrightarrow (C_6H_5)_3CNHC_6H_5 \qquad \text{(II)}$$

This simple addition to the anil linkage in benzophenone-anil has not so far been observed with phenylmagnesium bromide. Furthermore, when the reaction is forced by refluxing an ether–toluene mixture of the anil with phenyl-lithium, the reaction mixture yields triphenylmethylaniline. So far none of the o-phenylbenzohydrylaniline (I) has been isolated.

It appears reasonable to attribute the different reactions with phenylmagnesium bromide to steric influences, not alone of the benzophenone-anil but also of the Grignard reagent. For example, the Grignard reagent is an equilibrium mixture containing, in part,[8] the following components.

$$2C_6H_5MgBr \rightleftharpoons (C_6H_5)_2Mg + MgBr_2 \qquad \text{(III)}$$

If diphenylmagnesium is the more effective reactant with the anil, then it might be expected that its greater molecular volume, when compared with the simpler phenyl-lithium, would significantly increase the already marked steric effects of the phenyl groups accumulated about the anil linkage in benzophenone-anil. This remains to be determined with related compounds. For the present, it may serve as a working basis to interpret different reactions of these, and other, organometallic compounds in reactions with compounds like naphthalic anhydride.[9] This would hardly serve as a sole explanation, for we are undoubtedly concerned with essential differences in reactivity independent of steric effects.

Just prior to the receipt of proof, an article [Bergmann and Rosenthal, *J. prakt. Chem.*, 135, 267 (1932)] appeared describing the formation of *o*-phenylbenzohydrylaniline from the interaction of benzophenone-anil and phenyl-lithium. It is quite probable that their product (m. p. 144°) was triphenylmethylaniline (m. p. 147°) and not o-phenylbenzohydrylaniline (m. p. 144°). The hydrochloride obtained by them melted at 186°, whereas the hydrochloride of o-phenylbenzohydrylaniline[6] melts at 182.5°. The mistaken identity is somewhat understandable in view of the related melting points.

Experimental Part

The general procedures were those employed previously with Grignard reaction rate studies.[1b,c] All reactions were effected in a nitrogen atmosphere, and during refluxing the solutions were maintained under a slight positive pressure exerted by nitro-

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(7) Kohler and Nygaard, THIS JOURNAL, **52**, 4128 (1930). See also Kohler and Baltzly, *ibid.*, **54**, 4016 (1932).

(8) Gilman and Fothergill, *ibid.*, **51**, 3149 (1929).

(9) Wittig, Leo and Wiemer, *Ber.*, 64, 2405 (1931). For other illustrations of different reactions see Ziegler and Zeiser, *ibid.*, **63B**, 1847 (1930); *Ann.*, 485, 174 (1931); Bergmann, Blum-Bergmann and von Christiani, *ibid.*, 488, 80 (1930).

gen and controlled by a mercury trap. The ether used throughout the experiments was freshly distilled under anhydrous conditions from a solution of phenylmagnesium bromide. A 10% excess of reactant was used. The times were recorded when one-half of the organometallic compound had been added (in some cases the addition cannot be made rapidly because of the violent refluxing of the ether) and to a negative color test[10] with a 10-cc. portion of the reaction mixture.

In experiments with n-butyl-lithium, 20 cc. of 1 *N* solution (0.02 mole) was added to the reactant in 90 cc. of ether. In all other cases 15 cc. of a 1.33 *N* solution of organometallic compound was added to the reactant in 95 cc. of ether. The effect of concentration on reaction velocities has been examined," and the slight change in concentration during the addition of n-butyl-lithium is not significant because an immediate reaction was observed with this compound. Inasmuch as n-butyl-lithium reacts with ether at a moderate rate, it was used directly after its preparation. Apropos of the stability of n-butyl-lithium, it is interesting to note that in a blank qualitative experiment, 0.02 mole in 110 cc. of ether was refluxed for four hours, then allowed to stand for fifteen hours and finally refluxed for eight hours to yield a solution such that one cc. gave a strong color test. After setting aside this solution for three weeks a 1-cc. sample gave a negative color test, but a 10-cc. sample gave a fairly strong color test. At the end of four weeks, a 10-cc. sample gave a negative test.

Earlier rate studies with some RMgX compounds were confirmed. The present results, given in Table I, were obtained with different concentrations than those used previously. Preliminary experiments having shown the marked differences in reaction velocities, the first samples were generally removed after an elapsed time of four minutes. The maximum times given with the less reactive RMgX compounds as 8+ hours means simply that the time required for complete reaction is in excess of eight hours and not necessarily between eight and nine hours.

Miscellaneous Rate Observations—In order to determine the effect of long-chained organometallic compounds on relative reactivities, n-lauryl-lithium (n-$C_{12}H_{25}Li$)[11] was compared with n-laurylmagnesium bromide in reactions with benzonitrile. After refluxing a solution of 0.03 mole of n-lauryl-lithium with 0.033 mole of benzonitrile in a total ether volume of 220 cc. for four minutes, a negative color test was observed. Under corresponding conditions, n-laurylmagnesium bromide gave a strong positive test after refluxing for three hours. In both cases the solutions were clear yellow in color and free of precipitate. Accordingly, the length of the carbon chain is without essential influence on the relative rates of reaction of the two types of compounds.

Nitrobenzene and benzophenone are known to react promptly with phenylmagnesium bromide. They react at once with phenyl-lithium, the former giving a black reaction mixture and the latter a white precipitate. n-Butylmagnesium bromide reacts at once with ethyl cinnamate in a (0.02:0.011) ratio, and at once with nitro-*p*-xylene in a (0.02:0.0067) ratio.

The only anomalous compound so far encountered is n-valeronitrile. With 0.022 mole of this nitrile and 0.02 mole of either phenylmagnesium bromide or phenyl-lithium the time is 6+ hours. However, with 0.044 mole of the nitrile and 0.02 mole of either phenylmagnesium bromide or phenyl-lithium the time is eight minutes. The absence of significant time differences with essentially equimolecular proportions of reactants warrants a further study of nitriles.

Reaction between **Nitriles and Organolithium** Compounds.—To 3.21 g. (0.022 mole) of *p*-dimethylaminobenzonitrile in 56.5 cc. of ether was added 0.02 mole of methyl-lithium in 53.5 cc. of ether. The color test at the end of four minutes was negative.

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[10] THIS JOURNAL, 47, 2002 (1925).

[11] The authors are grateful to Mr. E. A. Zoellner for this organolithium compound and for other assistance.

TABLE I

REACTIONS WITH C_6H_5MgBr, C_6H_5Li, n-C_4H_9MgBr AND n-C_4H_9Li

				0.02 Mole C_6H_5MgBr			0.02 Mole C_6H_5Li		
					Appearance			Appearance	
No.	Reagent	G.	Mole	Time, hours	Soln.	Ppt.	Time, hours	Soln.	Ppt.
1	C_6H_5CN	2.27	0.022	1.3	Colorless	White	0.07 –	Red	None[a]
2	$C_6H_5CH_2Cl$	2.78	.022	8+	Colorless	None	2.4	Colorless	White
3	$C_6H_5N{=}NC_6H_5$	4.00	.022	8+	Red	Yellow	0.07 –	Green	Black[b]
4	$(C_2H_5)_2SO_4$	3.39	.022	8+	Colorless	White	.23	Colorless	White
5	$C_6H_5CH{=}NC_6H_5$	3.98	.022	8+	Yellow	None	.07	Yellow	None[c]
6	$(C_6H_5)_2C{=}NC_6H_5$	5.65	.022	8+	Yellow	None	7 ± 1	Green	Black
7	$C_6H_5CH{=}CHCO_2C_2H_5$	1.94	.011	1.6	Yellow	None	0.07 –	Yellow	White
8	1,2,4-$C_6H_3(CH_3)(NO_2)$-(CH_3)	1.113	.0067	1.3	Red	None	.07 –	Red	None
9	Furfural	2.11	.022	0.07 –	Yellow	White	.07 –	Yellow	None
10	$(CH_3)_3CCOCH_3$	2.20	.022	0.07 –	Colorless	None	.07 –	Yellow	None

				0.02 Mole n-C_4H_9MgBr			0.02 Mole n-C_4H_9Li		
					Appearance			Appearance	
No.	Reagent	G.	Mole	Time, hours	Soln.	Ppt.	Time, hours	Soln.	Ppt.
1	C_6H_5CN	2.27	0.022	8+	Yellow	White	0.07 –	Orange	None
2	$C_6H_5CH_2Cl$	2.78	.022	8+	Colorless	None	.07 –	Colorless	White
3	$C_6H_5N{=}NC_6H_5$	4.00	.022	0.5	Red	Yellow	.07 –	Green	Black
4	$(C_2H_5)_2SO_4$	3.39	.022	8+	Colorless	White	.11	Colorless	White
5	$C_6H_5CH{=}NC_6H_5$	3.98	.022	8+	Yellow	None	.07 –	Yellow	None

[a] The yield of benzophenone was 60%.

[b] When 0.011 mole of azobenzene was refluxed with 0.02 mole of phenyl-lithium, a negative color test was not obtained after several hours. The proposed mechanism for this reaction is incomplete and is being investigated further.

[c] The yield of benzohydrylaniline was 67%. It was identified by a mixed melting point determination of its hydrochloride.

The excess nitrile was then removed by the addition of 0.004 mole of methyl-lithium The yield of *p*-dimethylaminoacetophenone was 45%. A corresponding reaction between 0.011 mole of *p*-dimethylaminobenzonitrile and phenyl-lithium also took place promptly (no color test in four minutes), to yield 56% of p-dimethylaminobenzophenone. Identification of this ketone was supplemented by the preparation of its oxime.

To 2.93 g. (0.022 mole) of p-methoxybenzonitrile in 56.5 cc. of ether was added 0.02 mole of methyl-lithium in 53.5 cc. of ether, and a negative color test was observed after four minutes. The yield of *p*-methoxyacetophenone was 75%. In a corresponding reaction with 2.93 g. (0.022 mole) of p-methoxybenzonitrile in 90 cc. of ether and 0.02 mole of phenyl-lithium, the negative color test was observed at the end of thirty minutes; the yield of *p*-methoxybenzophenone was 85%; and characterization was completed by the preparation of the oxime.

Benzophenone-anil and Phenyl-lithium.—To 25.7 g. (0.1 mole) of benzophenone-anil in 120 cc. of ether was added 0.1 mole of phenyl-lithium in 80 cc. of ether. The greenish-black reaction mixture was refluxed for six hours, and then worked up in a customary manner to yield 71% of triphenylmethylaniline which was identified by the method of mixed melting points. In another experiment, the product obtained by refluxing 0.45 mole of benzophenone-anil with 0.05 mole of phenyl-lithium in an ether-toluene mixture for one hour at 95° was triphenylmethylaniline in a 68% yield. The reactants in this latter experiment were mixed at about 95°.

The authors gratefully acknowledge a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for assistance in this study.

Summary

1. A study of the relative reactivities of organolithium and organomagnesium compounds shows that the former undergo more rapid reaction with a selected number of typical reactants. Also, n-butyl-lithium is more reactive than phenyl-lithium.

2. Some compounds, like p-dimethylaminobenzonitrile and *p*-methoxybenzonitrile, which do not react with the Grignard reagent, undergo prompt reaction with methyl- and phenyl-lithium to give the expected products.

3. The unusual 1,4-addition of phenylmagnesium bromide to the lateral-nuclear conjugated system in benzophenone-anil is not shown by phenyl-lithium which adds normally to the anil linkage, both under mild and forced conditions, to give triphenylmethylaniline. An explanation based, in part, on the different molecular volumes of the two organometallic compounds is proposed to account for the differences in behavior with sterically hindered functional groups.

AMES, IOWA

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PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 340]

The Nitration of Para-Cresol and of Para-Cresyl Carbonate in the Presence of Sulfuric Acid[1]

BY HOWARD J. LUCAS AND YUN-PU LIU[2]

The addition of sulfuric acid during the nitration of some aromatic compounds is known to influence the ratio of meta to ortho–para substitution. This is especially true of aromatic amines such as aniline, of which the ortho–para directing NH_2 group is converted, by salt formation, into the meta directing NH_3 group. An explanation has been advanced[3] for this behavior on two grounds, *viz.*, (1) the addition of the proton to the lone electron pair of the nitrogen atom greatly increases the electron attraction of the entire group, and (2) the blocking off of the lone pair prevents any possibility of addition formation at this point with the reagent and therefore of subsequent rearrangement to ortho and para positions on the ring.

According to Vorlander, Robinson, Ingold and others[4] the most strongly meta-directing groups are the positive poles directly attached to the benzene ring. Thus phenyltrimethylammonium nitrate is nitrated exclusively in the meta position[6] and many other compounds of similar type yield meta derivatives almost exclusively on nitration; among these may be mentioned diphenyl iodonium nitrate,[6] triphenylantimony dinitrate,[7] triphenylbismuth dinitrate[8] and diphenyllead dinitrate.[9]

The change in the ortho–para directive influence of the NH_2 group to the meta orienting influence of the NH_3X group through salt formation has been ascribed to the ionization of the salt to give a positive ion in which substituents take the meta position because of the positive charge carried by the NH_3^+ group. Fliirscheim and Holmes[4d] found that the addition of ammonium sulfate to the nitrating mixture of nitric and sulfuric acid decreased the yield of the meta isomeride formed during the nitration of benzyldiethylamine while Pollard and Robinson[10] observed similar effects in the nitration of benzylpiperidine. In these cases the added salts depress the ionization of the salt undergoing nitration and thus cause a decrease in the meta directive power of the positive pole.

Since the oxygen atom resembles the nitrogen atom in the formation of

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(1) Paper presented at the Denver Meeting of the American Chemical Society, August, 1932.

(2) China Foundation Fellow.

(3) Lucas. THIS JOURNAL, 48, 1827 (1926).

(4) (a) Vorländer, *Ber.*, **52**, 262 (1919); (b) Allan, Oxford, Robinson and Smith, J. *Chem. Soc.*, 401 (1926); (c) Goss, Ingold and Wilson, *ibid.*, 2440 (1926); (d) Fliirscheim and Holmes, *ibid.*, 1562 (1926); (e) Ingold, *Annual Reports Chem. Soc.*, *23*, 130 (1926).

(5) Vorlander and Siebert, *Ber.*, **52**, 283 (1919).

(6) Vorländer and Biichner, *ibid.*, **58**, 1898 (1926).

(7) Morgan and Micklethwaite, *J. Chem. Soc.*, *99*, 2286 (1911)

(8) Vorlander and Schroedter, Ber., **58**, 1900 (1928).

(9) Vorlander and Spreckels, *ibid.*, **58**, 1900 (1928).

(10) Pollard and Robinson. *J. Chem. Soc.*, 2770 (1927).

TABLE I

EFFECT OF SULFURIC ACID UPON NITRATION OF *p*-CRESOL IN GLACIAL ACETIC ACID (24 G.)

Expt.	*p*-Cresol, g.	HNO_3 1.42 g.	H_2SO_4 1.84 g.	Molal ratio H_2SO_4/*p*-Cresol	Temp., °C.	Time, min.	Products in grams					Percentage of yield				Ratio *m*/*o*
							p-Cresol	*o*-NO_2[a]	*m*-NO_2[b]	di-NO_2[c]	*p*-Cr	*o*-NO_2[a]	*m*-NO_2[b]	di-NO_2[c]	Total	
I	2.7	1.5	0	0	−15 to −20	5–10	1.1550	1.947	trace	0.0186	42.8	51.0	trace[d]	0.40	94.2	0
II	2.7	1.0	1.0	0.41	0	30	1.1840	0.3893	0.1144	.0188	43.9	10.2	3.1[e]	.40	57.6	.28
III	2.73	1.0	2.0	0.81	−15 to −20	3–5	1.9450	.3654	.1131	.0129	71.3	9.5	2.9	.30	84.0	.29
IV	2.72	1.0	3.0	1.22	−15 to −20	3–5	1.6990	.3214	.1226	.0080	62.5	8.4	3.2	.20	74.3	.36
V	2.7	1.0	4.0	1.63	−15 to −20	3–5	1.4540	.4147	.1512	.0006	53.9	10.9	4.0	.02	68.8	.36
VI	2.7	1.0	6.0	2.45	−15 to −20	30	1.1562	.3729	.1631	.0019	42.8	9.8	4.3	.04	56.9	.43
VII	2.7	1.0	7.0	2.70	−15 to −20	3–5	2.1180	.2730	.1258	.0042	78.5	7.1	3.3	.10	89.0	.45
VIII	2.7	1.5	8.0	3.27	−15 to −20	3–5	1.7655	.2737	.1263	.0049	65.4	7.2	3.3	.10	76.0	.45
IX	2.7	1.5	9.0	3.50	−15 to −20	3–5	1.8205	.2603	.1385	.0043	67.4	6.8	3.6	.10	77.9	.52
X	2.7	1.5	10.0	4.08	−15 to −20	3–5	2.2015	.2408	.1686	.0017	81.5	6.3	4.4[f]	.03	92.2	.69
XI	2.7	1.5	12.0	4.70	−15 to −20	3–5	1.8740	.2484	.1818	.0012	69.4	6.5	4.8	.02	80.7	.73
XII	2.7	1.5	25.0	9.80	−15 to −20	60	1.4041	.7520	.5880	.0010	52.1	19.7	15.4	.02	87.2	.78

[a] Nitro group ortho to the hydroxyl. [b] Nitro group meta to the hydroxyl. [c] Nitro groups ortho to the hydroxyl. [d] No benzoate of *m*-nitro-*p*-cresol obtained. [e] Benzoate of *m*-nitro-*p*-cresol obtained in 61% yield. [f] Benzoate of *m*-nitro-*p*-cresol obtained in 84% yield.

onium salts, the nitration of a phenol in the presence of varying amounts of sulfuric acid might be expected to yield different ratios of meta derivatives. It has been shown recently that the addition of sulfuric acid in the nitration of benzaldehyde and of ethyl benzoate leads to increased production of the meta derivative.[11]

For this work p-cresol was selected since it is known to form two addition compounds with sulfuric acid, *viz.*, $2C_7H_8O \cdot H_2SO_4$, m. p. 11.0°, and $C_7H_8O \cdot 2H_2SO_4$, m. p. 93.5°.[12] If these compounds are ionized the electronic formulas are, for the former, $2CH_3C_6H_4:\overset{H}{O}:H^+, SO_4^=$; and for the latter, $CH_3C_6H_4:\overset{H}{\underset{H}{O}}:H^{++}, 2HSO_4^-$. The presence of a positive charge on the former would presumably increase the proportion of the meta isomer produced on nitration while the presence of a doubly positive charge on the latter would be expected to have an even greater effect. Any influence of added acid, due to salt formation alone, might be expected to carry through to the esters of p-cresol, and for that reason the carbonate of p-cresol was also nitrated under varying conditions.

The results obtained with *p*-cresol by nitrating in glacial acetic acid solution are shown in Table I, and those with *p*-cresyl carbonate and fuming nitric–sulfuric acid mixture are shown in Table II.

TABLE II

EFFECT OF SULFURIC ACID UPON THE NITRATION OF *p*-CRESYL CARBONATE

Expt.	Molal ratio Carbonate:	Molal ratio HNO_3: 2.5% N_2O_5	Molal ratio H_2SO_4 5% SO_3	Temp., °C.	Nitration products, per cent. *p*-Cresol	*o*-NO_2	di-NO_2	Total *o*-NO_2	*m*-NO_2	Total	Ratio *m*/*o*
I	1	1.9	0	−10	39.7	32.8	0.2	33.2	3.8	76.5	0.1
II	1	1.9	1.2	0 to −5	37.4	2.7	14.2	31.1	7.3	61.6	0.2
III	1	2.2	2.9	0	27.7	8.8	4.8	18.4	28.8	70.1	1.6
IV	1	2.2	3.9	0	8.9	14.2	6.7	27.6	44.5	74.3	1.6
V	1	2.2	4.4[a]	0	19.0	12.0	4.4	20.8	34.3	69.7	1.7
VI	1	2.2	5.5[b]	0	5.2	9.1	9.8	28.7	52.4	76.5	1.8
VII	1	2.1	6.2	0 to −5	5.8	6.7	11.7	30.1	65.3	89.5	2.2
VIII	1	2.1	8.2	−5 to −10	1.5	5.8	7.2	20.2	48.6	63.1	2.4
IX	1	2.1	10.3	−5 to −10	3.6	6.2	9.9	26.0	61.6	83.3	2.4

[a] 95% H_2SO_4. [b] 90% H_2SO_4.

When using fuming sulfuric and nitric acids p-cresol undergoes rapid decomposition and satisfactory results cannot be obtained. The addition of glacial acetic acid cuts down the undesirable side reactions so that, by working rapidly, one can obtain a fair amount of nitration products. On the other hand, the nitration of the carbonate proceeds much more smoothly and can be carried out with the nitric and sulfuric acids alone.

The results obtained in these nitration experiments are shown graphically

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(11) Baker and Moffitt, *J. Chem. Soc.*, 314 (1931); Baker and Hey, *ibid.*, 1226 (1932).

(12) Kendall and Carpenter, THIS JOURNAL, 86, 2498 (1914).

in the figure where the molal ratio of nz-nitro to *o*-nitro[13] isomer is plotted against the ratios of sulfuric acid to the compound undergoing nitration. In the case of p-cresol, only the ortho isomer is formed when there is no sulfuric acid present, but when the sulfuric acid–cresol ratio is one-half, the meta–ortho ratio is approximately one-fourth. As more sulfuric acid is added the meta–ortho ratio rises, at first slowly, then more rapidly, and finally reaches a maximum where further addition of acid changes the meta–ortho ratio but little.

In the case of *p*-cresyl carbonate the meta–ortho ratio is 0.1 at zero concentration of sulfuric acid. It changes slowly at first as acid is added, then more rapidly, and finally approaches a maximum.

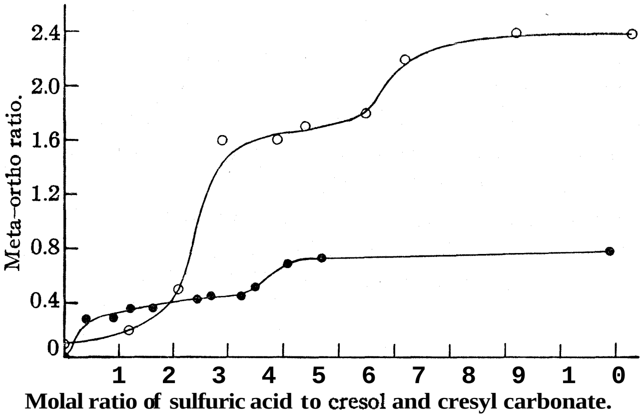

Fig. 1.—○, **Nitration of *p*-cresyl carbonate; ●, nitration of *p*-cresol.**

Interpretation of the Results.—Increase in the amount of the meta isomer on the addition of sulfuric acid can be accounted for on the basis of oxonium salt formation. It is to be expected that the rate of increase at first would be greater in the case of *p*-cresol since the weakly basic properties of its oxygen atom should exceed the even weaker basic properties of the carbonate. The initial rapid increase in the meta-ortho ratio during the nitration of p-cresol corresponds to its conversion into the addition compound, $2CH_3C_6H_4OH \cdot H_2SO_4$. Additional sulfuric acid has little effect until the second addition compound, $CH_3C_6H_4OH \cdot 2H_2SO_4$, is formed. Since the latter is partly dissociated, an excess of sulfuric acid is necessary for the complete conversion of the first into the second. The break in the curve after three moles of sulfuric acid have been added probably corresponds to this change. Finally, the maximum value of 0.8 in the meta–

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[13] Since the discussion centers about the hydroxyl group the derivatives are named in reference to it, rather than to the methyl group. Thus 2-nitro-4-hydroxytoluene is here called *m*-nitro-*p*-cresol and 3-nitro-4-hydroxytoluene is called o-nitro-p-cresol.

ortho ratio indicates that even when completely converted into the disulfate compound more ortho than meta is formed.

In the case of the carbonate the rapid rise in the meta–ortho ratio comes only after approximately two moles of sulfuric acid have been added. Since the carbonate is a weaker base than the cresol the oxonium reaction on each phenolic oxygen should require a higher ratio of sulfuric acid, probably one of acid to each oxygen atom. The resulting compound, $(C_7H_7O)_2CO{\cdot}2H_2SO_4$, would probably be unstable and require an excess of sulfuric acid for its complete formation. The rapid rise in the meta–ortho ratio above this point probably corresponds to the conversion of the small amount of uncombined carbonate into the oxonium complex. The second rapid rise above five moles of sulfuric acid probably corresponds to the complete transformation of the first complex into a second, *viz.*, $(C_7H_7O)_2CO{\cdot}4H_2SO_4$. Further addition of sulfuric acid brings about little additional change.

The increase in the meta orienting influence of the oxygen atom through salt formaticn is probably due to its greater attraction for the electron pair which joins it to ring carbon, a condition associated with an increase in the residual kernel charge of the oxygen atom.[14] It is evident that this charge is greater, the greater the degree of ionization of the oxonium complex, since the hydrogen atoms act as bonds in the undissociated molecules. One would expect a progressive increase in the residual kernel charge of the oxygen atom in the following radicals: OH, OH_2X, OH_3X_2, OH_3X^+, OH_3^{++}. On the basis of the positive pole theory the last two should be exclusively meta orienting. The production of the ortho isomer, even in a large excess of sulfuric acid, seems to indicate that a part of the complex is un-ionized and that the nitration of this gives the ortho as well as the meta isomer. It is reasonable to assume, therefore, that on the addition of sulfuric acid the orienting influence of the hydroxyl group suffers modification in the same way as the amino group, but to a less extent.

Experimental

Materials.—–Eastman *p*-cresol No. P 449, m. p. 33–34", was twice distilled under reduced pressure and the portion boiling at 102–102.5° and 22 mm. was collected. It melted at 36.0°. This was converted into the carbonate by dissolving in sodium hydroxide solution and passing in carbonyl chloride.[15] After crystallizing from alcohol it melted at 113°.

3-Nitro-p-cresol, 3-nitro-4-hydroxytoluene (called o-nitro-p-cresol in this paper) was prepared by nitrating 108 g. (1 mole) of *p*-cresol with a mixture of 135 g. of concd. nitric acid (1.4 moles), 200 g. of concd. sulfuric acid (2 moles), and 500 ml. of water at 5–10° The solution was extracted with ether, the ether was evaporated and the solid was twice steam distilled, m. p. 32.0–32.5°. It analyzed 99.3% pure with standard titanous sulfate and 99.0% pure with standard bromide–bromate solution.

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[14] Latimer and Porter, THIS JOURNAL, 52, 206 (1930).

[15] Holleman and Hoeflake, *Rec. trav. chim.*, 36, 271 (1916).

2-Nitro-*p*-cresol, 2-nitro-4-hydroxytoluene (called m-nitro-p-cresol in this paper) was prepared by nitrating *p*-cresyl carbonate and saponifying the resulting nitrocarbonate according to the method of Copisarow.[16] The yellow, odorless needles from alcohol melted at 78.5° and analyzed 99.5% pure with standard titanous sulfate and 99.4% pure with standard bromide-bromate.

3,5-Dinitro-*p*-cresol, 3,5-dinitro-4-hydroxytoluene, was prepared by nitrating 36 g. (0.33 mole) of p-cresol at 30–40° with a mixture of 135 g of concd. nitric acid (1.4 mole) and 200 g. of concd. sulfuric acid (2 moles). The reaction mixture was steam-distilled and the residue of crude product was recrystallized from alcohol several times, using norite for decolorizing, m. p. 85.0°. This was found to be 99 3% pure by analysis with standard titanous sulfate and with standard bromide–bromate.

The benzoate of 3-nitro-p-cresol was prepared in quantitative yield by the action of benzoyl chloride upon 3-nitro-p-cresol dissolved in pyridine. After one crystallization from alcohol the yield of fairly pure crystals was 90%. A second crystallization yielded colorless flakes melting at 96.0°. Reduction with standard titanous solution gave 5.4% N; theoretical for $C_{14}H_{11}O_4N$, 5.45% N.

The benzoate of 2-nitro-p-cresol was prepared as above, in approximately the same yield. It crystallized from alcohol in pale yellow needles melting at 90°. Reduction with standard titanous solution gave 5.42% N; theoretical for $C_{14}H_{11}O_4N$, 5.45% N.

Nitration.—The operations were carried out in a 20-cm. test-tube provided with a mercury-sealed stirrer, a dropping funnel to admit the nitrating mixture, and an exit tube carrying a calcium chloride tube to prevent moisture from entering. The test-tube was immersed in a freezing mixture of ice and hydrochloric acid at −15 to −20°. To 2.7 g. (0 025 mole) of p-cresol dissolved in a mixture of 18 g. of glacial acetic acid and varying amounts of c. p. concd. sulfuric acid was added a mixture of 1 to 1.5 *g*. of c. p. concd. nitric acid (0.01 to 0.017 mole) and 6 g. of glacial acetic acid, usually during three to five minutes. The mixture was at once poured onto ice and worked up according to the procedure described under purification. It was found that when the cresol was nitrated with a mixture of nitric and sulfuric acids alone only small amounts of nitrocresols could be obtained since considerable oxidation took place; but in glacial acetic acid the undesirable reactions were so cut down that the nitro compounds could be obtained. However, it was necessary to keep the mixture at −12 to −20° and to shorten the time of addition; otherwise there was a fairly large amount of non-phenolic material produced. Because of the deficiency of nitric acid, only a part of the p-cresol was nitrated. The amount of unreacted cresol could be decreased by increasing the time (see Expt. VI, Table I), but more non-phenolic compounds were formed. However, the tendency to undesirable side reactions seemed to drop off at high sulfuric acid ratios since in Expt. XII good yields of products were obtained even though the mixture stood for sixty minutes.

The nitration of the *p*-cresyl carbonate was carried out in the same apparatus, as follows. To 4.83 g. (0.02 mole) of the carbonate dissolved in varying amounts of fuming sulfuric acid containing 5.0% of sulfur trioxide was added 1.9 to 2.2 g. of fuming nitric acid (0.03–0.035 mole) containing 2 5% of nitrogen pentoxide. The temperature was kept at 0 to −10° during the nitration and for three hours afterward; the mixture was then allowed to stand overnight and in the morning it was poured onto a mixture of 30 g. of chopped ice and an amount of sodium carbonate sufficient to neutralize about two-thirds of the sulfuric acid. The precipitated material was filtered onto a Gooch crucible and saponified by refluxing for two to three hours with a solution of 6 g. of sodium carbonate in 60 ml. of water.[16] The solution containing the sodium salts of *p*-cresol and its nitration products was filtered from a small amount of flocculent material, acid was added to the filtrate and this solution was worked up as described under purification

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(16) Copisarow, J. *Chem. Soc.*, 251 (1929).

below, except that the solid o-nitro-p-cresol and *m*-nitro-*p*-cresol were dried to constant weight.

Purification and Separation of Reaction Products.—The aqueous acid solutions resulting from the nitration of p-cresol and from the hydrolysis of the nitrated *p*-cresyl carbonate were extracted with ether several times. The ether phase was then extracted with dilute **(0.5 to 1.0 N)** sodium hydroxide. Following this extraction the ether phase was usually colored by the presence of non-phenolic compounds resulting from oxidation. This was discarded. Dilute sulfuric acid was added to the aqueous phase, another ether extraction followed, and after evaporation of the ether the residue was steam distilled, unchanged p-cresol and o-nitrocresol coming over, m-nitro- and dinitrocresol remaining behind The distillate was extracted with ether, the ether phase was dried with anhydrous sodium sulfate and then evaporated. The residue was dissolved in **100** ml. of glacial acetic acid. Solutions resulting from the nitration of *p*-cresol were analyzed by titration with standard titanous sulfate solution[17] and those from the carbonate, with standard bromide–bromate solution.[17] The residue of *m*-nitro- and dinitrocresol, along with some non-phenolic material, was dissolved in ether, which was then extracted with dilute sodium hydroxide solution. This phase was filtered, dilute sulfuric acid was added, and the cresols dissolved out by ether. The ether phase, after drying with anhydrous sodium sulfate, was evaporated off and the residue was dissolved in **100** ml. of glacial acetic acid. Solutions coming from the nitration of p-cresol were analyzed by reduction with standard titanous solution, followed by titration with standard bromide–bromate solution. Those from the nitration of the carbonate were analyzed with bromide–bromate.

The separation by steam distillation of p-cresol and o-nitro-p-cresol from m-nitro- and di-nitro-p-cresol under the conditions used gave satisfactory results with a known mixture, as shown below:

	Distillate		Residue	
	p-Cresol g.	o-nitro-p-cresol, g.	m-nitro-p-cresol, g.	dinitro-p-cresol, g.
Weight taken	0.3001	2.0011	0.2466	0.0214
Weight recovered	.2981	1.9871	.2478	.0215

Analysis.—The determination of p-cresol and of o-nitro-p-cresol in a mixture of these two obtained by the steam distillation of the reaction product from the nitration of p-cresol was done by titrating one aliquot of the glacial acetic acid solution with standard titanous sulfate, following the procedure described by Francis and Hill[17] for the use of titanous chloride in determining nitro compounds in alcoholic solution, and by titrating a second aliquot first with an excess of titanous sulfate and second with standard bromide–bromate, following again the procedure of Francis and Hill. The use of glacial acetic acid is preferable to alcohol since the latter slowly reacts with the bromide–bromate solution.[18] From the amount of titanous solution required the amount of nitro compound can be calculated readily, and from the titanous and bromate titrations the amount of unchanged cresol is easily calculated. The data below show the results obtained with a known mixture:

ANALYSIS OF *p*-CRESOL (1.5250 G.) AND *o*-NITRO-*p*-CRESOL (0.3650 G.) DISSOLVED IN 100.0 ML. OF GLACIAL ACETIC ACID, BY REDUCTION AND BROMINATION

Soln., ml.	$Ti_2(SO_4)_3$ (0.00628 *N*), ml.	$KBrO_3$ (0.1022 *N*), ml.	*o*-Nitro-*p*-cresol Taken, g.	Found, g.	Error, %	*p*-Cresol Taken, g.	Found, g.	Error, %
2	9.01	13.73	0.00730	0.00727	−0.83	0.0305	0.03021	−1.0
2	9.04	13.78	,00730	.00729	− .50	.0305	.03028	−0.7

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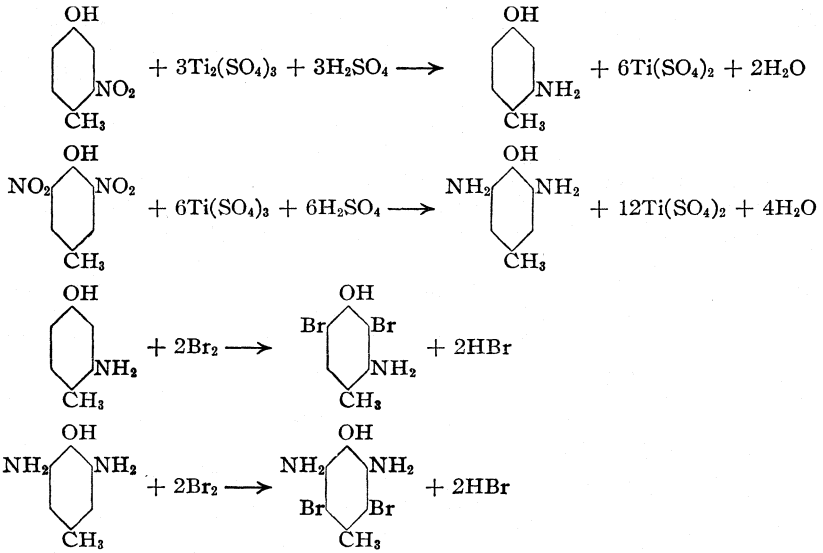
(17) Francis and Hill, THIS JOURNAL, 46, 2498 (1924).

(18) Buxton and Lucas, *ibid.*, 60,249 (1928).

In the same way the mixture of m-nitro- and dinitro-*p*-cresol can be analyzed, the calculations being based upon the equations



When *a* is equivalents of titanous sulfate and b is equivalents of bromine used up, the weight of m-nitro- (x) and of dinitro-p-cresol (y) can be calculated by means of the two equations

$$x = 76.56 - 153a;\quad y = 198a - 49.5b$$

The data below show the results obtained with a known mixture.

ANALYSIS OF *m*-NITRO-*p*-CRESOL (0.2025 G.) AND DINITRO-p-CRESOL (0.0200 G.) DISSOLVED IN 50.0 ML. OF GLACIAL ACETIC ACID, BY REDUCTION AND BROMINATION

Soln., ml.	$Ti_2(SO_4)_3$ (0.00528 *N*) ml.	$KBrO_3$ (0.0536 *N*), ml.	m-Nitro-p-cresol Taken, g.	Found, g.	Error, %	Dinitro-*p*-cresol Taken, g.	Found, g.	Error, %
2	11.62	4.28	0.00810	0.00814	+0.5	0.00080	0.00079	−1.2
2	11.60	4.27	.00810	.00814	+ .4	.00080	.00079	−1.2

The reaction products from the nitration of *p*-cresyl carbonate were analyzed by bromination alone. In this case it was necessary to know the weight of solid material and this was obtained by complete evaporation of the ether solutions, followed by desiccation over concd. sulfuric acid for one or two days. With known mixtures bromination gave fairly satisfactory results.

ANALYSIS OF *p*-CRESOL (1.0835 G.) AND *o*-NITRO-*p*-CRESOL (2.1406 G.) DISSOLVED IN 250 ML. OF GLACIAL ACETIC ACID, BY BROMINATION ALONE

Soln., ml.	$KBrO_3$ (0.1346 N), ml.	*p*-Cresol Taken, g.	Found, g.	Error, %	o-Nitro-p-cresol Taken, g.	Found, g.	Error, %
10	20.15	0.04334	0.04279	−1.3	0.08562	0.08601	+0.5
10	20.18	.04334	.04290	−1.0	.08562	.08590	+ .4

The calculations above were based upon the fact that p-cresol reacts with two moles of bromine and the o-nitro derivative with only one. In the equations x is amount of *p*-cresol, y is amount of *o*-nitro-*p*-cresol, a is equivalents of bromine used and w is weight of the sample in grams.

$$x = 41.80a - 0.547w$$
$$y = 1.548w - 41.80a$$

ANALYSIS OF *m*-NITRO-*p*-CRESOL (0.3621 G.) AND DINITRO-*p*-CRESOL (0.1284 G.) IN 50 ML. OF GLACIAL ACETIC ACID; BY BROMINATION ONLY

		m-Nitro-*p* cresol			Dinitro-*p*-cresol		
Soln., mi.	$KBrO_3$ (0.1346 N), ml.	Taken, g.	round, g.	Error, g.	Taken, g.	Found, g.	Error. %
10	14.16	0.07242	0.07304	+0.8	0.02568	0.02506	– 2.4
10	14 14	.07242	07302	+ .8	02568	.02508	– 2.4

These calculations are based upon the fact that *m*-nitro-*p*-cresol reacts with two moles of bromine and the dinitro compound with none. The calculations are made according to the equations below in which x is weight of m-nitro- and y is weight of dinitro-*p*-cresol.

$$x = 38.25a$$
$$y = w - 38.25a$$

Experimental Results.—The results of the nitration of p-cresol in glacial acetic acid solution and of the nitration of p-cresyl carbonate are given in Tables I and II. It is from these data that the curves shown earlier were constructed.

In the nitration of p-cresol there was always a deficiency of nitric acid. The small amount of dinitro compound was assumed to be the isomer in which both nitro groups were ortho to the hydroxyl. Benzoylation of the residue non-volatile with steam from Experiment II gave an amount of the benzoate of m-nitro-p-cresol equivalent to 61% of the meta compound found by analysis and the residue from Experiment X gave 84%. None of this benzoate could be obtained from Experiment I.

Since p-cresyl carbonate undergoes nitration with greater difficulty, it was necessary to use a mixture of fuming nitric and fuming sulfuric acid. Here again the dinitro-p-cresol was assumed to be 3,5-dinitro-4-hydroxytoluene. Such an assumption probably involves an error, since the dinitro compound may in part be the 2,5- or even the 2,6- isomer. If the former is present then the meta–ortho ratio should be less than the one calculated, while if the latter is present this ratio should be greater. It is possible that the error from this source is not great since these two effects counteract each other.

Summary

Nitrations of p-cresol and of p-cresyl carbonate have been carried out in the presence of sulfuric acid in amounts varying from 0 to 10 moles of acid per mole of organic compound. It was found in the case of p-cresol that the ortho directive power of the hydroxyl group decreased as sulfuric acid

increased, and that more and more of the entering nitro group took up a position meta to the hydroxyl. However, a maximum value of about 0.8 was reached for the meta–ortho ratio. This change in directive power is ascribed to the salt-forming property of the oxygen atom of *p*-cresol. The predominating tendency toward ortho substitution, even when a large excess of acid is present, probably arises from the fact that the oxonium salt is in part un-ionized.

In the case of *p*-cresyl carbonate, increase in the amount of sulfuric acid likewise increased the meta–ortho ratio. It is assumed that here also oxonium salt formation is responsible for the change.

These changes in orientation are entirely analogous to the modification in the orientation of amino and substituted amino groups by the addition of sulfuric acid.

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The Preparation of Some Structurally Related Monoguanidines

BY CHARLES E. BRAUN

Introduction

In a study of the relationship between guanidine structure and hypoglycemic activity it became necessary to prepare the following series of structurally related monoguanidines: a-phenylguanidine sulfate, benzylguanidine sulfate, phenylaminoguanidine hydrochloride, *p*-aminophenylguanidine sulfate, n-hexylguanidine sulfate, cyclohexylguanidine hydrochloride, o-tolylguanidine hydrochloride, m-tolylguanidine sulfate, p-tolylguanidine hydrochloride, a-methyl a-phenylguanidine hydrochloride and β-phenylethylguanidine sulfate. The first four were prepared as described by previous investigators.[1]

The detailed syntheses of the Latter seven are recorded here for the benefit of those interested in the field. While the nitrate salts of *o*-tolylguanidine and *p*-tolylguanidine have been described,[2] no record of their hydrochlorides could be found.

Since the compounds were synthesized for the purpose of studying their physiological reactions, special emphasis was placed upon purity, and no attempts were made to produce maximum yields. The hydrochloride and sulfate salts were selected to obtain greater water solubility than might be expected with the free bases or the nitrate salts. The results of the physiological investigation of these compounds, which is in progress, will be reported separately.

(1) Smith, THIS JOURNAL, **51**, 476 (1929); Davis and Elderfield, ibid., 64, 1499 (1932). Pellizzari, *Gazz* chim *ital.*, 21,330 (1891); Braun, THIS JOURNAL, **54**, 1511 (1932).

(2) Meister, Lucius and Bruning, German Patent 172,979; Kampf, Ber., **87**, 1683 (1904)

Experimental

***n*-Hexylguanidine Sulfate.**—*n*-Hexylamine was prepared by the reduction of *n*-capronitrile (Eastman practical) with sodium and absolute alcohol—m. p. hydrochloride salt, 219'.

14.5 g. (0.143 mole) of n-hexylamine and 21.0 g. (0.151 mole) of S-methyl isothiourea sulfate in 60 cc. of water were heated under reflux at 100° for five hours. The crystals obtained upon cooling the reaction solution were filtered off, washed with dry ether and air dried. The crude salt, when dry. was treated with boiling absolute alcohol, boneblacked (norite), and filtered hot. To the cold alcoholic solution was added sufficient ether to cause permanent turbidity. Upon standing in an ice chest crystals of the sulfate deposited. These were filtered off, washed with dry ether and dried at 100" *in* vacuo. After three recrystallizations from absolute alcohol a n-hexylguanidine sulfate was obtained which melted at 210–212°

The purified salt was white, crystalline, easily soluble in cold water and hot absolute alcohol, but insoluble in anhydrous ether. The final yield (purified salt) was 5.0 g. or 18.2%.

Anal. Calcd. for $C_7H_{17}N_3 \cdot 0.5H_2SO_4$: S, 8.34. Found: S, 8.37 (as $BaSO_4$).

Cyclohexylguanidine Hydrochloride.—Cyclohexylamine hydrochloride was prepared by passing dry hydrogen chloride into a cold solution of cyclohexylamine (Eastman) in anhydrous ether—m. p. cyclohexylamine hydrochloride, 204–205°.

Ten grams (0.074 mole) of cyclohexylamine hydrochloride and 4.5 g. (0.107 mole) of cyanamide (Eastman) in 50 cc. of absolute alcohol were heated under reflux at 100° for six hours. The solution was reduced to about half its volume under atmospheric pressure, after which, upon cooling, a crystalline compound deposited. The latter was filtered off, washed with ether and dried. The crude material (10.4 *g.)* melted over a wide range, 158–194°. The entire batch of this crude was extracted twice with boiling acetone, washed with ether, and dried at 100° *in* vacuo. The hydrochloride after recrystallization from boiling absolute alcohol melted at 224–226°.

The purified cyclohexylguanidine hydrochloride was white, crystalline, readily soluble in cold water and in hot alcohol but insoluble in ether and in boiling acetone. The yield (purified salt) was 8.4 g. or 64.0%.

Anal. Calcd. for $C_7H_{16}N_3Cl$: Cl, 19.96. Found: Cl, 19.92 (as AgCl).

***o*-Tolylguanidine** Hydrochloride.—o-Toluidine hydrochloride was prepared by passing dry hydrogen chloride into a solution of o-toluidine (Eastman practical) in anhydrous benzene—m. p crude o-toluidine hydrochloride, 205–206°.

Forty-five grams 10.314 mole) of o-toluidine hydrochloride (m. p. 205–206") and 18.0 g. (0.430 mole) of cyanamide (Eastman) in 100 cc. of absolute alcohol were heated under reflux at 100° for six hours. When the solution was concentrated to about one-third its volume the concentrate, a viscous sirup, set to an almost solid mass under vigorous agitation The solid was filtered off, washed with a small volume of anhydrous ether, and dried at room temperature in uacuo. The crude material (24 5 g.) was dissolved in 450 cc. of boiling acetone, boneblacked and the solution filtered hot. The hydrochloride was precipitated in crystalline condition from the cold acetone solution by slow addition of ether. After filtration and washing with ether, it was dried at 78° *in* vacuo. A second acetone-ether purification produced an analytically pure compound which melted at 133–135°

The purified o-tolylguanidine hydrochloride was white, crystalline, soluble in cold water and hot acetone, but insoluble in ether. The yield (purified salt) was 18.4 g. or 31.6%.

Anal. Calcd. for $C_8H_{12}N_3Cl$: Cl, 19 11. Found Cl, 19.00 (as AgCl).

***m*-Tolylguanidine** Sulfate.—Ten grams (0.10 mole) of m-toluidine (Eastman practical) and 9 g. (0.065 mole) of S-methyl isothiourea sulfate suspended in a mixture of 10 cc. of alcohol and 10 cc of water were heated under reflux at 100° for about thirty hours. A yellowish solid which had formed after cooling was filtered off, ground under a mixture of alcohol and ether and dried at room temperature under vacuum. The alcohol–ether extraction removed practically all of the color and left a crude sulfate (5 0 g.) which melted at 210–212°. The crude material was dissolved in a large volume of hot 95% alcohol, boneblacked and filtered hot. The addition of ether to the cooled alcoholic solution precipitated the sulfate as a white, crystalline powder, easily soluble in cold water but insoluble in ether. The pure compound melted at 215–217°. The yield (purified salt) was 4.0 g. or 31.1%, calculated on 0.065 mole of m-toluidine

Anal. Calcd. for $C_8H_{11}N_3 \cdot 0.5H_2SO_4$: S, 8.09. Found: S, 8.13 (as $BaSO_4$).

***p*-Tolylguanidine** Hydrochloride.—Forty-two grams (0.29 mole) of *p*-toluidine hydrochloride (m. p. 243°) and 18 g. (0.43 mole) of cyanamide (Eastman) in 43 cc. of absolute alcohol were heated under reflux at 100° for six hours. When the solution was concentrated to about one-half its volume, the concentrate after cooling. set to an almost solid mass of crystals. These were filtered off, ground under cold acetone refiltered, washed with cold acetone and ether, and dried at room temperature *in vacuo* The crude material (17 g.) was white and melted at 133–135".

The crude product was dissolved in 90 cc of boiling absolute alcohol boneblacked, and filtered hot. After reducing the volume of the solution, a small amount of a white crystalline compound deposited This was filtered off, washed with ether and dried at room temperature. The dry material weighed 1.3 g. and melted at 245–247". Analytical data established this compound as the hydrochloride salt of p-tolylbiguanide.

Anal. Calcd for $C_9H_{14}N_5Cl$: Cl, 15.57. Found: Cl, 15 68 (as AgCl).

These data are not in agreement with those of Beutel,[3] who reported that *p*-tolylbiguanide hydrochloride had the formula $C_9H_{14}N_5Cl \cdot 0\ 5H_2O$, and that the anhydrous salt melted at 235°, uncorrected.

The alcoholic filtrate. after removal of the *p*-tolylbiguanide salt, was concentrated at 100°. The concentrate when cool, deposited 11.7 g. of crystalline material which, when dry, melted at 130–133°. This impure hydrochloride was treated with 200 cc. of cold absolute alcohol, in which it was almost completely soluble After filtration the solution was concentrated, cooled and treated with ether until a permanent turbidity existed Upon standing in an ice chest the solution deposited a batch of white crystals which were filtered off, washed with ether and dried at 78° *in vacuo.* The purified *p*-tolylguanidine hydrochloride was white, crystalline, soluble in water and hot absolute alcohol but insoluble in ether. It melted at 136–137". The yield (purified salt) was 9 5 g. or 17.4%.

Anal. Calcd for $C_8H_{12}N_3Cl$: Cl, 19.11. Found: Cl, 19 06 (as AgCl).

α-Methyl-α-Phenylguanidine Hydrochloride.—Methylaniline hydrochloride was prepared by passing dry hydrogen chloride into a cold solution of methylaniline (Eastman, b. p. 81–82" (14 mm.)) in benzene.

48.5 g (0.34 mole) of methylaniline hydrochloride (m. p. 121°) and 17 g. (0.41 mole) of cyanamide (Eastman) in 30 cc. of absolute alcohol were heated under reflux at 100° for ten hours. After cooling, the solution deposited a large quantity of white crystals which were filtered off, washed with ether and dried at room temperature *in vacuo.* The crude hydrochloride weighed 43.8 g. and melted at 206–208°

Purification was effected by dissolving the salt in boiling absolute alcohol, boneblacking, filtering hot and adding sufficient ether to the cold filtrate to produce perma-

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(3) Beutel, Ann.. 310, 344 (1900).

nent turbidity. After the alcohol-ether solution had stood in an ice chest, the purified hydrochloride crystallized out, was filtered off, washed with ether and dried *at* 100° in *vacuo.* The pure α-methyl α-phenylguanidine hydrochloride was white, crystalline, soluble in cold water and hot alcohol but insoluble in ether. It melted at 217–218°. The yield (pure salt) was 22.3 g. or 35.3%.

Anal. Calcd. for $C_8H_{12}N_3Cl$: Cl, 19.11. Found: Cl, 19.03 (as AgCl).

β-Phenylethylguanidine Sulfate.—Twenty grams (0.165 mole) of β-phenylethylamine (b. p. 76.5–78° (8 mm.)) and 20 g. (0.144 mole) of S-methylisothiourea sulfate in 250 cc. of water were heated at 100° for four hours. After evaporation of most of the water a crystalline material deposited. which was filtered off, washed with small volumes of acetone and ether and air dried. The crude material melted rather abnormally. It softened at 80°, appeared to evolve a gas between 95–105°, and then solidified. The second solid melted without decomposition at 170–172°. These observations suggested that possibly the original solid was a hydrate which lost its water of crystallization at 95–105°, leaving an anhydrous compound which melted at 170–172°. The original and final substances gave positive sulfate reactions.

Recrystallization from boiling absolute alcohol produced large glistening crystals, soluble in cold water and giving a positive sulfate reaction. The material from absolute alcohol softened at 60–65°, appeared to evolve a gas at 95° and then solidified. The second solid melted without decomposition at 168–173°. A second recrystallization from absolute alcohol produced identical results. The crystalline compound was air dried, and its sulfur content determined in order to prove or disprove the idea that the compound, crystallized from alcohol, is β-phenylethylguanidine sulfate with alcohol of crystallization. The analytical data established this point.

Anal. Calcd. for $(C_9H_{13}N_3 \cdot 0.5H_2SO_4) \cdot C_2H_5OH$: S, 6.19. Calcd. for $C_9H_{13}N_3 \cdot 0.5 H_2SO_4$: S, 7.56. Found: S, 6.65 (as $BaSO_4$).

The remainder of the crystalline material was heated for six hours at 78° *in vacuo* and then at 100° in *vacuo* to drive off the alcohol of crystallization. The compound, after heating, lost its glistening crystalline appearance and became dull. It melted at 175–177". Repeated recrystallizations from absolute alcohol followed by heating *in vacuo* failed to raise the melting point. The sulfur content of the compound melting at 175–177° was 7.63%, which established it as β-phenylethylguanidine sulfate. In one experiment a final melting point of 180.5–181° was observed but subsequent trials failed to confirm this. The purified sulfate was white, very soluble in water and hot absolute alcohol, only slightly soluble in acetone and insoluble in ether. The yield (purified salt m. p. 175–177°) was 12.3 g. or 40.3%, calculated on 0.144 mole of β-phenylethylamine.

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The author wishes to thank Professor Homer Adkins of the University of Wisconsin for his kindness in supplying the β-phenylethylamine, and the American Cyanamid Company for the thiourea used in this work. He is also pleased to acknowledge the technical assistance of Mr. Robert T. Conner of the University of Vermont.

Summary

1. The methods of preparation and general properties of the following monoguanidines have been described: n-hexylguanidine sulfate, cyclohexylguanidine hydrochloride, o-tolylguanidine hydrochloride, *m*-tolyl-

guanidine sulfate, *p*-tolylguanidine hydrochloride, a-methyl α-phenylguanidine hydrochloride and β-phenylethylguanidine sulfate.

2. A corrected formula and melting point for *p*-tolylbiguanide hydrochloride have been reported.

BURLINGTON, VERMONT

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[CONTRIBUTION FROM THE TECHNICAL UNIVERSITY, DELFT, HOLLAND]

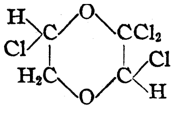
Derivatives of Dioxane

BY J. BÖESEKEN, F. TELLEGEN AND P. COHEN HENRIQUEZ

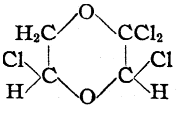
In a previous communication[1] we mentioned the first results of a research on the chlorination of 1,4-dioxane. 2,3-Dichlorodioxane, the first product of chlorination, was separated; the chlorine atoms proved to be very mobile as they are in all a-chloro ethers. With sodium ethylate we isolated the 2,3-diethoxydioxane, while with glycol the two isomeric naphthodioxanes (1,4,1′,4′-tetroxadecahydronaphthalene). These investigations were continued in different directions.

A. The Action of Chlorine on Dioxane.—Neither repeated distillation nor investigation of the products of hydrolysis of the first fraction gave any indication of the existence of monochlorodioxane. The investigation of the mechanism of the first stage of the chlorination is still being continued.

On chlorinating dichlorodioxane, it appeared that chlorine is rapidly absorbed. The first time the chlorination was continued for sixteen hours at 130–150° and the product was carefully fractionated. The first fraction, boiling below 102° (15 mm.), appeared to have a chlorine content corresponding with tetrachlorodioxane. Hydrolysis by means of boiling water produced glycolic aldehyde. Subsequent treatment with dinitrophenylhydrazine gave the dinitrophenylhydrazone of glycolic acid and the dinitrophenylosazone of glycolic aldehyde. The quantity of these precipitates was in accordance with the expectation, based on the decomposition of one of the following tetrachlorodioxanes



Form 1



Form 2

Butler and Cretcher[2] succeeded, after a chlorination of twelve hours, in the isolation of a crystalline asymmetrical and two isomeric symmetrical tetrachlorodioxanes besides the liquid asymmetrical one, just mentioned. In the higher-boiling fractions of the product obtained by the chlorination of dichlorodioxane during sixteen hours, only very little oxalic acid could

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(1) *Rev. trav. chim.*, 60, 909 (1931); *Proc. Acad. Sci.*, **34**, 631 (1931).

(2) Butler and Cretcher, THIS JOURNAL, 64, 2987 (1932).

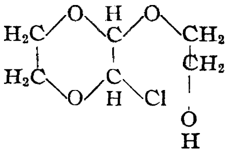
be detected after decompn. with water, so that we may conclude that tetrachlorodioxane, with all the four chlorine atoms at one side of the molecule, is hardly formed. The odor of the chlorinated dichlorodioxane reminds us of acid chlorides, but ammonia did not yield an amide and cold silver nitrate solution did not yield more than a very little precipitate, so that with this chlorination very little or no acid chloride is formed.

The second time the chlorination was continued for twenty-four hours. The reaction product was repeatedly fractionated in the apparatus of Widmer;[3] the liquid was divided in seven fractions: but none of these fractions had a constant boiling point. The first fraction had a chlorine content almost agreeing with pentachlorodioxane and the last fraction a chlorine content little less than hexachlorodioxane.

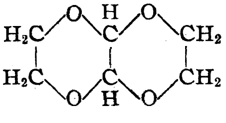
The third time we chlorinated for about fifty hours at 110° and also at 50°. After fractionation it was possible to obtain crystals in some fractions by cooling. The second fraction of the latter chlorination yielded beautiful big crystals of a hexachlorodioxane, the last fractions of the other chlorination mixed crystals of two compounds, containing more chlorine than the hexachlorodioxane.

The hexachlorodioxane, melting at 89.5–91.0° and having the odor of camphor, is not destroyed by boiling with silver nitrate or potassium hydroxide solution in alcohol. The liquid part of the fractions appeared to be hygroscopic in a high degree. With gaseous ammonia they yielded immediately in dry ether solution a bulky white precipitate, which is also the case with cold silver nitrate solution, so that probably the ring structure is broken with the formation of acid chloride.

B. Reactions of **Dichlorodioxane.**—As we previously mentioned dichlorodioxane forms by boiling with glycol two isomeric naphthodioxanes. We have also to mention a publication of Donciu.[4] Donciu isolated out of the product, obtained by the action of chlorine on glycol, crystals to which he credited the formula 1a. Treatment of this compound with sodium gave a product, m. p. 134–135°, to which he assigned formula 2a, and which he also could obtain by the action of glycol on glyoxal.



Form **1a**



Form 2a

As the compound to which Donciu credited formula 2a is identical with the higher melting isomeride of naphthodioxane, the formulas suggested by him appear to be the right ones. The melting points of the two isomerides, in as pure a condition as we could get, are 111–112° and 135–136°. After

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(3) **Widmer, Dissertation,** Zürich, 1925.

(4) **Donciu,** *Sitzber. Kais. Acad. Wiss.*, [C] *4*, 2b, 7 (1895).

careful sublimation of the mixture of the two isomers in the apparatus of Kempf, the melting point of the sublimate was observed with a microscope on a electrically heated object table.[5] All crystals appeared to melt near the melting point of the eutectic mixture of the mixture (87°), so that it is highly probable that the difficulty of the separation is due to the formation of mixed crystals; also Donciu met with great difficulties in the purification of the higher melting isomeride. Within a short time we hope to describe the properties of the isomerides more fully and also of the reaction product of trimethyleneglycol, which consists of at least two isomers.

Dichlorodioxane reacts with pyrocatechol in boiling xylene; crystals of m. p. 74–76' were obtained (see formula 3).[6]

The action of benzyl alcohol results in the greasy-looking white crystals of formula 4, m. p. 66–68'.

It seemed interesting to investigate the action of the esters of the tartaric acids on dichlorodioxane. Theoretically ten isomers are possible. With the ethyl ester of d-tartaric acid we obtained only one of the three possible compounds, m. p. 93.3–94.7°, for which $[\alpha^{22}_{\mathrm{D}}]$ in a 0.8% alcoholic solution was determined to be —0.30'. The composition agreed with formula 5.

The ester of the anti-tartaric acid also reacts with dichlorodioxane, but we did not succeed in separating from the reaction product a pure compound.

Dichlorodioxane does not react with boiling acetic acid; the reaction proceeds, however, if a few drops of strong sulfuric acid are added. By pouring out the reaction mixture in water an amorphous precipitation occurs of a white compound insoluble in all normally applied organic solvents. This compound is not the diacetate of dioxane, which can conveniently be prepared by the action of potassium acetate in a solution of acetic acid on dichlorodioxane. The diacetate of dioxane (see formula 6), white crystals of m. p. 104–105.5°, shows a remarkable stability toward dilute potassium hydroxide or acid solution.

The reaction of dichlorodioxane with sodium iodide is noteworthy, because of the liberation of iodine. In boiling acetone iodine is liberated and precipitation of sodium chloride occurs. It might seem that dioxene is formed. When we try to prepare the dioxene by removing the chlorine atoms by light metals in solutions of high-boiling solvents, the metal is coated with a black tar, which can be due to polymerization of the dioxene and which prevents further reaction.

Experimental Part

Reaction with (1) **Pyrocatechol.**—Eleven grams of catechol and 15.6 g of dichlorodioxane were boiled for about a week in 40 cc. of dry xylene. After distillation of the xylene in *vacuo* a brown, sticky substance remained which gave a crystalline mass by distillation in high vacuum. Three recrystallizations in ether furnished crystals of

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(5) Derx, Dissertation, Delft, 1922.

(6) *Cf.* R. Summerbell and R. Christ, THIS JOURNAL, **54**, 3777 (1932).

m. p. 74–76°. The pale yellow color is probably due to impurity. The amount of the compound was 5 g.

Anal. Calcd.: mol. wt., 194; C, 62.1; H, 5.1. Found: mol. wt., 190; C, 62.3, 62.2; H, 5.3. 5.1.

(2) **Benzyl Alcohol.**—7.5 g. of benzyl alcohol was heated with 5.0 g. of dichlorodioxane until no more hydrogen chloride was liberated. The brown reaction product was distilled in high vacuum. The oil thus obtained crystallized for the larger part in about four days. Recrystallizations in ligroin and alcohol gave 2 g. of flat, greasy-looking crystals, m. p 66–68', very soluble in all common organic solvents and insoluble in water.

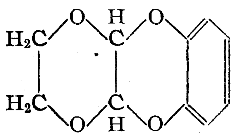
Anal. Calcd.: C, 72.0; H, 6.7. Found: C, 72.1, 72.3; H, 6.4, 6.5.

(3) **Diethyl Ester of d-Tartaric Acid.**—6.7 g. of di-ethyl ester of d-tartaric acid and 5.0 g. of dichlorodioxane were heated until the production of hydrogen chloride stopped. The brown reaction product was distilled in high vacuum The fraction distilling between 130 and 150° crystallized. Three recrystallizations from alcohol gave needle-like crystals of m. p. 93.3–94.7°, which are but sparingly soluble in ether and alcohol (less than 2%) at 20'; $[\alpha^{22}_{D}]$ −0.30 for a 0.8% alcoholic solution. The amount of the pure substance was 2.0 g.

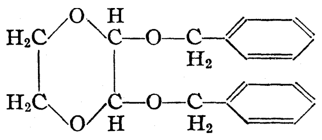
Anal. Calcd.: C, 49.5; H, 6.2. Found: C, 48.8; H, 6.1.

(4) **Potassium Acetate.**—19.1 g. of anhydrous potassium acetate and 15.1 g. of dichlorodioxane were dissolved in 70 cc. of dry acetic acid. The reaction was initiated by heating and proceeded vigorously with evolution of heat. The precipitated potassium chloride was filtered and the acetic acid was distilled off in *vacuo*. The brown oily substance thus obtained was distilled in high vacuum. After recrystallization from ether we obtained 4.8 g. of fine, white needle-shaped crystals, m. p. 104–105.5'.

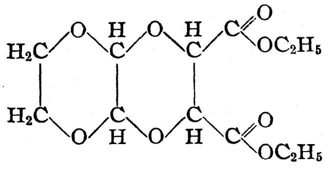
Anal. Calcd.: C, 47.1; H, 5.7. Found: C, 47.1; H, 5.9.



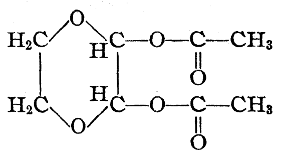
Form 3



Form 4



Form 5



Form 6

Tetrachlorodioxane.—Thirty grams of dichlorodioxane was chlorinated during sixteen hours at 130–150°. The fraction boiling below 102" (15 mm.) led to the following analyses: chlorine found, 63.1, and 63.1%; calcd., 63.1%. 6.4 mg. of the liquid was heated with 20 cc. of water in a closed tube in boiling water. Destruction with boiling water in an Erlenmeyer flask with reflux condenser is not possible, for the small quantity of the liquid creeps into the condenser, so that it is not attacked by the water. After the hydrolysis the quantity of the precipitate with dinitrophenylhydrazine was determined; this proved to be 18.0 mg., while the theoretically calculated amount for formulas 1 or 2 is 19.0 mg. A test with pure dichlorodioxane under the same conditions showed that the amount of hydrazone experimentally found does not exceed 95% of the calculated value. These analyses, in addition to the fact that glycolic aldehyde can be indicated after the hydrolysis with water and that dinitrophenylhydrazine produces two different precipitations enable us to conclude that the choice must be between the formulas 1 and 2.

After chlorinating 50 g. of dichlorodioxane during twenty-four hours (140°), we obtained a mixture with a chlorine content of about 5.5% for 1 dioxane, out of which we could not separate any constant boiling fraction nor any crystals, notwithstanding the fact that we submitted the liquid to very careful repeated fractionation.

Hexachlorodioxane.—Forty grams of dichlorodioxane was chlorinated for about fifty hours at 60°. From the second fraction hexachlorodioxane separated after cooling in ice (2 g., m. p. 89.5–91°).

Anal. Calcd.: C, 16.3; H, 0.7; Cl, 72.2; O, 10.8; mol. wt., 295. Found: C, 16.2; H, 0.9; Cl, 72.2; O, 10.8; mol. wt., 300.

The oxygen was determined by the direct method of ter Meulen, the mol. wt. by the method of Rast; all values are the average of at least two analyses. Forty grams of dichlorodioxane was chlorinated for about fifty hours at 110°. After distillation we obtained a crystalline residue, which was purified from brown impurities by distillation in high vacuum. The melting point of the mixture thus obtained was 54–60°.

Carefully fractionated precipitation by means of water, out of the alcoholic solution, was not adequate for the isolation of one of the components in pure condition; the compounds of which the mixture consists form mixed crystals. The chlorine content of the mixture is about 76%.

Once more we lay stress on the extreme stability of the hexachlorodioxane and the above-mentioned mixture of highly chlorinated products. The chlorine is not removed by boiling alcoholic potassium hydroxide or silver nitrate solution. The chemical investigation of the structure of these compounds will therefore prove to be very difficult if not impossible

Summary

By chlorinating dichlorodioxane we isolated one liquid asymmetrical tetrachlorodioxane and a hexachlorodioxane. Higher chlorinated products are under study. It is highly probable that by long duration of the chlorination the ring structure is broken through. There are no indications of the existence of mono-, tri- and pentachlorodioxane. The stability of the chlorinated dioxanes increases greatly with increasing chlorine content, the stability of the hexachlorodioxane being so great as to prevent the investigation of its structure. The reaction products of dichlorodioxane with pyrocatechol, benzyl alcohol, diethyl ester of d-tartaric acid, and potassium acetate are isolated; no isomerides are found by these compounds, which is remarkable in face of the fact that glycol and trimethyleneglycol both give isomerides.

DELFT, HOLLAND

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Notes

The Formation of Aromatic Ethers from p-Nitrofluorobenzene

By Morgan J. Rarick, R. Q. Brewster and F. B. Dains

In the course of an investigation on the oxidation of alcoholates with *p*-nitrofluorobenzene it was observed[1] that the fluorine atom is remarkably labile and reacts readily with alkaline solution of the alcohols or phenols with nearly quantitative formation of ethers. We now find that this substitution of p-nitrofluorobenzene for *p*-nitrochlorobenzene in the older method for the production of aromatic ethers results in a more rapid reaction and usually also a better yield. In addition some of the substituted diphenyl ethers can be obtained easily from phenolic compounds and P-nitrofluorobenzene which are produced from *p*-nitrochlorobenzene only with the greatest difficulty. Only rarely is the use of a catalyst necessary. Even with the nitrophenols, where Raiford and Colbert[2] found *p*-nitrochlorobenzene to produce almost no yields of the dinitrodiphenyl ethers, p-nitrofluorobenzene gives 70–80% of the theoretical amount.

Holleman and Beekmann[3] reported the ease with which 2,4-dinitrofluorobenzene reacts with sodium methylate to give 2,4-dinitroanisole, but in fluorobenzene itself they found the fluorine atom to be more firmly held to the benzene nucleus than chlorine. In 2-nitro-4-chlorofluorobenzene Swartz found the fluorine atom more easily replaced than chlorine.[4]

Experimental.—The production of ethers from p-nitrofluorobenzene is accomplished by three general methods as illustrated in the three following typical experiments.

4-Nitroanisole.—To a cooled solution of 3 g. of potassium hydroxide in 20 cc. of warm methyl alcohol was added 7 g. (0.05 mole) of p-nitrofluorobenzene and the mixture shaken. The immediate exothermic reaction was complete in about ten minutes, whereupon the mixture was poured into water and the 4-nitroanisole separated and crystallized from ligroin (b. p. 90–110°); yield 7 g. or 93%.

Ethyl, n-propyl, isopropyl, isoamyl, benzyl and phenylethyl alcohols and ethylene glycol behave[6] in the same manner and produce equally good yields of the ethers.

4-Nitrodiphenyl Ether.—To a cooled solution of 3 g. of potassium hydroxide in 15 g. of molten phenol was added 7 g. (0.05 mole) of p-nitrofluorobenzene and the mixture heated in an oil-bath at 150–160° for thirty minutes. The mixture was then poured into a dilute sodium hydroxide solution and the solid 4-nitrodiphenyl ether collected on a filter. It was recrystallized from alcohol or ligroin; yield 10 g. or 92%.

By a similar procedure equally good yields of the corresponding substituted diphenyl ethers were obtained by replacing the phenol with one of the three cresols, guiacol, hydroquinone monomethyl ether, *p*-chlorophenol, o-iodophenol, *p*-phenylphenol, *p*-*tert*-amylphenol and acetyl-p-aminophenol.

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(1) Continuation of the work of Dains, Suter and Kenyon. Dains and Suter. THIS JOURNAL, 50,2733 (1928); Dains and Kenyon, *ibid.*, 53,2357 (1931).

(2) Raiford and Colbert, Tars JOURNAL, 48,2660 (1926).

(3) Holleman and Beekmann, Rcc. trao. chim., 23, 249 and 254 (1904).

(4) Swartz, *Rcc.* trao. *chim.*, 35, 147 (1915).

(5) The ether obtained here is the mono-4-nitrophenyl ether of ethylene glycol.

4,4'-Dinitrodiphenyl Ether.—Nine grams (0.05 mole) of the dry potassium salt of *p*-nitrophenol was heated with 20 g. (13-g. excess) of *p*-nitrofluorobenzene and 0.2 g. of copper powder at 200° for one hour. The excess of p-nitrofluorobenzene was recovered by distillation in steam and the crude 4,4'-dinitrodiphenyl ether crystallized from ligroin; yield 11 g. or 85%.

The dry potassium salts of m-nitrophenol, salicylic aldehyde, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid, when substituted for the dry potassium salt of p-nitrophenol in the above procedure, produce approximately the same yields of the corresponding ethers.

The dry potassium salt of o-nitrophenol, however, gives only 30% of the theoretical amount.

Analyses.—Since some of the ethers prepared above are not recorded in the literature, their melting points and analyses are here reported.

ANALYSES

Ether	M. p., °C.	Nitrogen, % Calcd.	Found	
p-Nitrophenyl isopropyl ($C_9H_{11}O_3N$)	B. p. 276–277 at 738 mm.	7.73	7.70	
p-Nitrophenyl phenylethyl ($C_{14}H_{13}O_3N$)	56–57	5.76	5.80	
p-Nitrophenyl *m*-tolyl ($C_{13}H_{11}O_3N$)	63	6.11	6.12	
p-Nitrophenyl o-iodophenyl ($C_{12}H_8O_3NI$)	105	4.11	4.20	
p-Nitrophenyl *p*-phenylphenyl ($C_{18}H_{13}O_3N$)	120	4.81	4.85	4.89
p-Nitrophenyl *p*-*tert*-amylphenyl ($C_{17}H_{19}O_3N$)	60	4.92	4.95	4.99
p-Nitrophenyl *p*-acetaminophenyl ($C_{14}H_{12}O_4N_2$)	153	10.30	10.30	
p-Nitrophenyl m-nitrophenyl ($C_{12}H_8O_5N_2$)	123	10.77	10.84	10.87
2-(*p*-Nitrophenoxy)-benzaldehyde ($C_{13}H_9O_4N$)	112	5.76	5.83	5.96

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

RECEIVED NOVEMBER 12, 1932
PUBLISHED MARCH 7, 1933

The Preparation of Vinyl Iodide

BY JOHN SPENCE

Vinyl iodide is the one vinyl halide suitable for study because of its comparatively high boiling point and the absence of any marked polymerizing tendency. An improved method for the preparation of vinyl iodide was used whereby the time of preparation was reduced and the yield increased from 18 to 35%.[1]

Ethylene diiodide was prepared by passing a rapid current of ethylene through a number of flasks in series containing iodine dissolved in 80% alcohol in presence of a large excess of solid iodine. It was found advantageous to carry out this operation in the illumination supplied by a 500-watt lamp; 500 g. of iodine gave approximately 300 g. of product after the customary purification.

Vinyl Iodide.—To 282 g. (1 mole) of ethylene diiodide was added 334 cc. of 3 *N* sodium ethoxide. The distillate was collected at a temperature of

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(1) Baumann, *Ann.*, *163*, 319 (1872).

-30 to $-50°$. Distillation was continued with heating until no further separation of halide was observed on addition of a saturated solution of sodium chloride. Crude vinyl iodide was thus separated, washed with dilute sodium bisulfite solution, with water and finally dried over calcium chloride. On redistillation practically all the product passed over at a temperature of 56–56.5°. Approximately 50 g. was obtained. The refractivity was determined. Owing to the ease of oxidation of vinyl iodide the observations were made in an atmosphere of nitrogen.

SPECIFIC GRAVITY 2.037 (20°)

Line	Index of refraction	Molecular refraction (found)	Molecular refractiou (calcd.)
Hydrogen (α)	1.53232	23.365	23.546
Sodium (D)	1.53845	23.651	23.769
Hydrogen (β)	1.55186	24.153	24.209
Hydrogen (γ)	1.56468	24.495	24.706

CHEMISTRY LABORATORY OF
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NEW YORK CITY

RECEIVED OCTOBER 8, 1932
PUBLISHED MARCH 7, 1933

The Mechanism of the Reduction of Sulfonyl Halides by Phosphorus Tribromide

BY A. H. KOHLHASE[1]

In a recent paper, Hunter and Sorenson[2] have stated that "previous work[3] has shown that sulfonyl chlorides are not reduced by phosphorus tribromide." This is in error as Kohlhase showed (Table I and Experiment XI) that 3-nitro-6-methylbenzenesulfonyl chloride was reduced readily and in good yield to the corresponding disulfide. It is true that sulfonyl chlorides were reduced far less readily than the corresponding bromides.

Kohlhase had concluded that the thiols formed in two instances of the reduction of sulfonyl derivatives by phosphorus tribromide, resulted as follows

$$RSSR + PBr_3 \qquad (RS)_2\cdot PBr_3$$
$$(RS)_2\cdot PBr_3 + 4H_2O \longrightarrow 2RSH + 3HBr + H_3PO_4$$

Hunter and Sorenson concluded that the mechanism is

$$RSO_2Br \xrightarrow{PBr_3} RSBr \xrightarrow{PBr_3} RSPBr_4 \xrightarrow{4H_2O} 2RSH + 4HBr + 2H_3PO_4$$

This interpretation seems rather convincing but Kohlhase[3] showed that phenyl 3,5-dinitrobenzenethiosulfonate, treated with phosphorus tribromide and then with ether and water, gave a very good yield of 3,5-di-

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(1) Present address, Whipple, Arizona.

(2) Hunter and Sorenson, THIS JOURNAL, 54, 3368 (1932).

(3) Kohlhase, *ibid.*, 54, 2441 (1932).

nitrothiophenol. Here the intermediate formation of a sulfur bromide is hardly possible and the mechanism originally proposed by Kohlhase seems the only one available. It is quite probable that in these reductions of all RSO_2X derivatives by phosphorus tribromide, *both* mechanisms may be operative, the relative speeds depending on conditions and on the nature of R and X, although the mechanism of Hunter and Sorenson is undoubtedly the chief one in most cases where a thiol is produced.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED NOVEMBER 7, 1932
PUBLISHED MARCH 7, 1933

Notes on the Thompson–Oakdale Method for the Determination of Halogen in Organic Compounds

BY J. J. THOMPSON AND U. O. OAKDALE

The Thompson–Oakdale method* for the determination of halogen has been used with excellent results in hundreds of instances in our laboratories. However, the fact is not always recognized that the alkaline solution of the halide contains a considerable amount of sodium sulfite and consequently erroneous results may be obtained in the gravimetric estimation of the halogen due to the fact that the precipitated silver halide is apt to be contaminated, possibly with silver sulfide formed by decomposition of silver sulfite. This difficulty may be obviated in the following manner. The alkaline solution to which sodium arsenite has been added in accordance with the original directions is poured into a beaker, cooled thoroughly and after the addition of about 5 cc. of superoxol or perhydrol, to oxidize the alkaline sulfite to sulfate, the mixture is stirred and boiled for a few minutes. The solution is then cooled, acidified with nitric acid and the halide precipitated in the usual manner.

In view of our observations on the use of this method by students it seems necessary to emphasize the fact that *all* of the halogen, especially in the case of iodine, cannot be driven through the condenser into the alkaline solution unless the mixture in the Kjeldahl flask is boiled in such a manner that a continuous stream of steam passes through the apparatus for a short time.

The potassium persulfate used must always be tested for perchlorate since many commercial brands of persulfate contain this impurity. Potassium persulfate, free from perchlorate, is now available commercially (Mallinckrodt Chemical Works).

COLLEGE OF PHARMACY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

RECEIVED DECEMBBR 16, 1932
PUBLISHED MARCH 7, 1933

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(1) Thompson and Oakdale, THIS JOURNAL, **52**, 1195 (1930).

1-Propyl-2-iodoacetylene

BY THOMAS H. VAUGHN

When the densities and indices of refraction of the alkyl iodoacetylenes are plotted against molecular weight it becomes apparent that the values for these constants reported for propyl iodoacetylene by Grignard and Perrichon [*Ann. chim.*, 5, 5–36 (1926)] are seriously in error.

This compound has been prepared in this Laboratory in 77% yield by the action of iodine on pentinylmagnesium bromide according to the procedure outlined by Grignard and Perrichon and has been found to possess the following properties: b. p. 67.0–67.5' at 35 mm.; 75–77° at 51 mm.; γ_{25} 34.22 dynes/cm. (maximum bubble pressure method); [P], obs., 283.3; calcd., 281.3; n^{25}_{D} 1.52231, n^{10}_{D} 1.5310; d_{25} 1.6557; MR'_{D} calcd., 36.54; obs., 35.73. These values for the index of refraction and density lie on their curves as determined from the other members of the series.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED JANUARY 11, 1933
PUBLISHED MARCH 7, 1933

COMMUNICATIONS TO THE EDITOR

HYDROGENOLYSIS OF ALCOHOLS TO HYDROCARBONS

Sir:

Recently we have found a method for the preparation of certain hydrocarbons which were not readily available. The reaction involved is the hydrogenolysis of a primary alcohol according to the equation $RCH_2OH + 2H_2 = RH + CH_4 + H_2O$. The reaction proceeded smoothly with duodecanol-1, tetradecanol-1, octadecanol-1 and 3-cyclohexylpropanol-1, from which were obtained n-undecane [b. p. 189–190° (740 mm.), n^{25}_{D} 1.41641, n-tridecane [b. p. 84–85' (3 mm.), n^{25}_{D} 1.4250, m. p. −7–8°], n-heptadecane [b. p. 290–292° (738 mm.), n^{25}_{D} 1.4360, m. p. 20–21°], and ethylcyclohexane [b. p. 127–128° (738 mm.), n^{25}_{D} 1.43101. Similarly the diprimary glycol, decanediol-1,10, by the removal of both carbinol groups was converted into n-octane [b. p. 121–123° (742 mm.), n^{25}_{D} 1.39751.

Hydrogenolysis was accomplished by subjecting 40 to 50 g. of the alcohol or glycol for about five hours to the action of hydrogen (100 to 200 atmospheres) at 250° over a nickel catalyst. The reaction proceeded almost quantitatively and no product other than the indicated hydrocarbon was found in any case. In some experiments a small amount of the original alcohol or glycol was recovered. [The catalyst and apparatus have been described in THIS JOURNAL, 54, 4116 (1932), and Ind. Eng. *Chem.*, Anal. *Ed.*, 4, 342 (1932).]

Secondary alcohols also undergo hydrogenolysis but in this case the reaction involves the cleavage of a carbon to oxygen rather than a carbon to carbon bond, *i.* e., $R_2CHOH + H_2 = R_2CH_2 + H_2O$. This type of reaction giving a hydrocarbon of the same carbon content as the alcohol is not novel; in fact it has been regarded as the normal reaction for primary as well as secondary and tertiary alcohols. The reaction proceeds smoothly under the conditions described above. For example, cyclohexane (m. p. 4–5°, n_D^{25} 1.4260) and n-octane were the only hydrocarbons obtained by the hydrogenolysis of cyclohexanol and octanol-2.

The primary–secondary glycol octadecanol-1,12, $CH_3(CH_2)_5CHOH(CH_2)_{10}CH_2OH$, as would be anticipated from the results stated above, underwent carbon to oxygen cleavage at the secondary carbinol, and carbon to carbon cleavage at the primary carbinol, with the formation of *n*-heptadecane, $C_{17}H_{36}$. The glycol [293 g., m. p. 67–69°, b. p. 200–208° (4 to 5 mm.)] was obtained by hydrogenation of castor oil (500 g.) over copper–chromium oxide catalyst (35 g.) for nine hours at 250° under 200–300 atmospheres pressure. The product so obtained was not completely homogeneous, as evidenced by its physical constants and the fact that in addition to the main product, n-heptadecane, a small amount of an unidentified hydrocarbon was obtained in its hydrogenolysis.

The primary alcohols and decanediol-1,10 subjected to hydrogenolysis were prepared from the ethyl esters of the corresponding acids through the action of hydrogen over a copper–chromium oxide catalyst [THIS JOURNAL, 54,4678 (1932)]. Both of the steps in the conversion of an ester to a hydrocarbon containing one less carbon atom than the acyl group of the ester can be accomplished by using a mixture of the two catalysts, *i.* e., copper–chromium oxide and nickel. However, our experience indicates that it is preferable to carry out the operation in two stages since the water formed in the second step prevents the completion of the first reaction.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
BRUNO WOJCIK
HOMER ADKINS

RECEIVED JANUARY 23, 1933 PUBLISHED MARCH 7, 1933

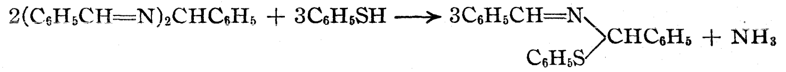
A NEW CONDENSATION REACTION OF THE THIOPHENOLS

Sir:

In view of the recent increase of interest in mercaptan chemistry, both in this country and abroad, we should like to report briefly upon a new reaction of the thiophenols, the investigation of which has been carried forward in this Laboratory during the past two years.

We have found that phenyl mercaptan itself, and many substituted thiophenols, as well as benzyl mercaptan, undergo condensation in boiling 1,4-dioxane solution with such condensed ammonia-aldehydes as hexamethylenetetramine and hydrobenzamide, only part of the nitrogen of the base being eliminated as ammonia. The products are crystalline substances (except in a very few cases) which may be considered as substituted trimethylamines. The following typical examples of the reaction will serve to illustrate

$$(CH_2)_6N_4 + 6C_6H_5SH \longrightarrow 2N(CH_2SC_6H_5)_3 + 2NH_3$$



$$2(C_6H_5CH{=}N)_2CHC_6H_5 + 3C_6H_5SH \longrightarrow 3\begin{matrix} C_6H_5CH{=}N \\ C_6H_5S \end{matrix}\!\!\big\rangle CHC_6H_5 + NH_3$$

The only analogous reactions which we have been able to find reported in the literature are those of hexamethylenetetramine with such weak acids as HCN [Eschweiler, Ann., 278, 230 (1894)] and N-nitromethylamine [Franchimont, Rec. *trav. chim.*, **29,** 355 (1910)], where a similar condensation takes place.

We are continuing our investigations and hope very shortly to be able to publish a detailed report of the work.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

GREGG DOUGHERTY
WENDELL H. TAYLOR

RECEIVED JANUARY 28, 1933 PUBLISHED MARCH 7, 1933

ON TEE MAXIMUM ROTATIONS IN THE HOMOLOGOUS SERIES OF α-BROMO ACIDS

Sir:

In the course of our work on the shift of the molecular rotations of members of homologous series, we were in need of resolving α-bromobutyric and α-bromocaproic acids to the maximum. The a-bromopropionic acid had already been resolved to the maximum of $[M]_D^{25}$ —43.6' by Ramberg [Ann., **370,** 234 (1909)] through the cinchonitie salt.

We succeeded in resolving the a-bromobutyric acid through its brucine salt to $[M]_D^{25}$ +59.62° and a-bromocaproic acid through its strychnine salt to $[M]_D^{25}$ −71.45°, thus showing that in this homologous series the values of the rotations of the individual members increase progressively. The progress in the case of the methyl esters was similar, being **83,** 92 and 104°, respectively, for the three esters.

These results were obtained nearly a year ago and remained unpublished for the reason that they were intended to be part of a comparative study of the rotations of the corresponding a-hydroxy and a-amino acids.

We wish to record the results at this time for the reason that in the current number of the Journal fur *praktische* Chemie there appeared an article by Ahlberg [*J. prakt. Chem.*, **135,** 335 (1932)] devoted exclusively to the resolution of α-bromobutyric acid. The author failed to accomplish resolution by means of the brucine salt, but by means of the strychnine salt obtained a value for the maximum rotation lower than ours and of opposite sign, namely, $[M]^{25}_{D}$ $-54.0°$.

It is interesting to note that through the strychnine salts both acids lead to active acids rotating in the same direction.

It may also be mentioned that a-bromobutyric acid had previously been resolved by Levene, Mori and Mikeska [J. *Biol. Chem.*, 75, 337 (1927)] to a degree somewhat higher than that of Ahlberg.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N Y.
P. A LEVENE

RECEIVED FEBRUARY 2, 1933 PUBLISHED MARCH 7, 1933

THE ROTATION OF MOLECULES OR GROUPS IN CRYSTALLINE SOLIDS

Sir:

In continuation of earlier studies of the possibility of rotation of molecules or groups in crystalline solids [Smyth and Hitchcock, THIS JOURNAL, 54,4631 (1932); *ibid.*, 55, in press (1933); Kamerling and Smyth, ibid., 55, 462 (1933)], the dielectric constants of hydrogen sulfide, ammonia and methyl alcohol have been measured from −190° to a few degrees above the melting points over a frequency range of 300 to 60,000 cycles. In solid hydrogen sulfide two sharp transitions are shown by the dielectric constant at −146.7' and −170.0°, in excellent agreement with the values just reported by Kemp and Denison [THIS JOURNAL, 55, 251 (1933)]. The dielectric constant of the solid, higher than that of the liquid, shows almost free molecular rotation above the lower transition. Below it, there appears to be practically no dipole rotation. The behavior of hydrogen sulfide is thus similar to that of the hydrogen halides and in marked contrast to that of ice.

The low dielectric constant of solid ammonia in contrast to the high value of the liquid and its small decrease with decreasing temperature show that the molecule behaves like large molecules, such as those of nitrobenzene, in possessing little or no rotation in the solid, thus differing from all the small molecules previously investigated by means of dielectric constants. The dielectric constant of solid methyl alcohol near the melting point is much lower than that of the liquid but high enough to give evidence of some dipole rotation, which decreases sharply at a transition point −114.0°, a value close to the average of those found from specific heat measurements, −115.7° by Kelley [THIS JOURNAL, 51, 180 (1929)], and −112.0' by Parks [ibid., 47, 338 (1925)]. Under conditions such that a glass is probably formed, a change of dielectric constant with frequency is found. Higher alcohols are being investigated in order to learn whether the dipole rotation is a limited rotation of the entire molecule or merely of the hydroxyl group.

FRICK CHEMICAL LABORATORY
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PRINCETON, NEW JERSEY
C. S HITCHCOCK
C. P SMYTH

RECEIVED FEBRUARY 8, 1933 PUBLISHED MARCH 7, 1933

THE ACTION OF BROMINE AND BUTADIENE

Sir:

Dr. H. Eyring has presented calculations in a paper given before the Section of Chemistry of the American Association for the Advancement of Science which indicated that addition of bromine to butadiene should be 1 4 rather than 1–2. The high energy of activation also indicated that the reaction should not occur in the gas phase. At the request of Doctors Taylor and Eyring, experiments have been made which show that on mixing gaseous butadiene and bromine in the ratio of 1–1 or 1–0.5 with from 15–20 volumes of nitrogen a reaction occurs and that crystals of the 1,4-dibromo-2-butene are formed. The melting point of the unpurified crystals was 53° (very sharp), which is identical with that reported in the literature. A mixture of the product with 1,2,3,4-tetrabromobutane melted from 30 to 48°. On carrying out the reaction in the same bulb which had been previously coated with paraffin, the rate of the reaction was very markedly reduced. This fact together with the observation that no fog or smoke formed in the uncoated reaction sphere leads to the conclusion that the reaction occurs on the surface. The kinetics of the reaction on glass and surfaces are being studied and details of the experiments will be reported later.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
G. B. HEISIG

RECEIVED FEBRUARY 20, 1933 PUBLISHED MARCH 7, 1933

THE ISOTOPE OF HYDROGEN

Sir:

With the aid of Dr. R. T. Macdonald I have been attempting to isolate various isotopes. Less than a month ago we turned our attention to the isotope of hydrogen. Our first experiments, employing a difference in overvoltage suggested by the work of Washburn and Urey, were so promising that we at once planned a systematic series of concentrations which has just been completed. This yielded water of specific gravity 1.035, which means that the heavy isotope constitutes one-third of all the water present. The refractive index of this heavy water is considerably lower than that of ordinary water, but exact figures cannot be given until the concentration has been accurately determined.

The separation of any isotope in sufficient quantity to permit investigation not only of its spectroscopic but also of its other chemical and physical properties suggests a wide range of interesting experiments but the isotope of hydrogen is, beyond all others, interesting to chemists. I believe that it will be so different from common hydrogen that it will be regarded almost as a new element. If this is true the organic chemistry of compounds containing the heavy isotope of hydrogen will be a fascinating study.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
GILBERT N. LEWIS

RECEIVED FEBRUARY 23, 1933 PUBLISHED MARCH 7, 1933

NEW BOOKS

Life and Experiences of a Bengali Chemist. By PRAFULLA CHANDRA RÂY. Chuckervertty, Chatterjee and Co., Ltd., 15 College Square, Calcutta, India, 1932. x + 557 pp. 14 X 22.5 cm.

This is an interesting and inspiring account of what a chemist's life can be. The first half of the book (Part I) is explicitly autobiographical. It describes in nearly chronological order: the author's early years on his father's estate in Bengal and at school in Calcutta; his student days under Crum Brown at Edinburgh; his return to become a professor of chemistry at Presidency College at Calcutta; his life as a teacher; his establishment during his spare time of the Bengal Chemical and Pharmaceutical Works, Ltd., now one of the great industrial concerns of India; his studies in the history of Hindu chemistry; his extensive experimental researches; finally, his manifold and multifarious activities in the public service.

The second half of the book (Part II) is only autobiographical; it contains numerous essays on educational, industrial, economic and social subjects. They not only serve to define the author's personality and point of view but they are also of the greatest interest, particularly to a far-away American, for the light they throw on the problems of present-day India. The author attacks scathingly the caste system that hangs as a millstone about India's neck and the ignorance and superstition of many of the Hindus. But his fiercest invective is launched against the spiritlessness and supineness of his fellow Bengali. As regards the British-Indian government he reaches, although by a different route and disagreeing with him in many vital points, the same position of non-cooperation championed by his compatriot Gandhi.

To the readers of this autobiography it is clear that, while Sir P. C. Rây has been a great scholar, chemist, teacher and administrator, these activities have been to him of secondary importance; he has been first, last and all the time a patriot—a Hindu and a Bengali. And he dedicates this account of his life, his opinions and his hopes for his country "To the Youth of India,"

ARTHUR B. LAMB

Kettenreaktionen. (Chain Reactions.) By KLAUS CLUSIUS. Verlag von Gebriider Rorntraeger, W **35,** Schoneberger Ufer 12a, Berlin, Germany, **3932.** iv + 73 pp. **24** figs. **16.5** X **25** cm. Price, to subscribers, RM. 9.60; separately, RM. **12.80.**

This is a brief review covering the field of gaseous chain reactions. The author starts by a description of the general characteristics of chain reactions and outlines the principles of their kinetic analysis. This is followed by a more detailed consideration of a few typical stationary chain reactions of the photochemical and thermal kind, to which some 20 pages is allotted. The remaining **30** pages are devoted to the non-stationary chain reactions, chiefly to the phenomena of the lower and the upper critical explosion pressure limits. Some rather disconnected bits of information on experimental technique are scattered through the text.

The presentation is far from exhaustive, but in the limited space used by the author one could hardly expect more material to be covered. The booklet will give a fair concept of the present status of the knowledge in the field of chain reactions to a reader already familiar with the principles of the kinetic treatment of reaction velocities. No serious mistakes have been noticed, but the reviewer feels that the fundamental work of Semenoff on the theory and experiment of the critical explosion limits and of non-stationary chains in general has not been sufficiently stressed by the author.

G. B. KISTIAKOWSKY

Elektrolyte. (Electrolytes.) By Dr. HANS FALKENHAGEN, Professor at the University of Cologne. Verlag von S. Hirzel, Konigstrasse **2,** Leipzig, Germany, **1932.** xvi + **346** pp. **104** figs. 17.5 X 25.5 cm. Price, Mk. 23: bound, Mk. **24.80.**

One of the most important and significant of recent advances in chemical theory has been the deeper insight into the nature of solutions of electrolytes which we owe to Debye and others who have been inspired by his leadership. Although others had conceived the idea that the fundamental weakness of the classical dissociation theory of Arrhenius was the neglect of the electric forces of attraction and repulsion between ions, Debye was the first to devise a mathematical technique adequate to predict quantitatively the effect of these forces on the measurable properties of solutions. This book is so permeated with the ideas of Debye that it is to be regretted that the publisher did not provide a portrait of Debye as a frontispiece.

Debye in a foreword says, "It is manifest that the time has now arrived to present the theory of electrolytes as developed up to the present time as a coherent whole and from a consistent point of view. That has been done in this monograph and I am grateful that such an expert as Falkenhagen, who himself has made such valuable contributions to the development of the theory, has undertaken this troublesome task."

The work opens with nearly one hundred pages devoted to fundamental definitions and a discussion of the strength and weaknesses of the older classical theory and the activity concept. Then follows a systematic mathematical development of the new theory in a manner which is clearer and easier to follow than it is in the scattered original literature. The seventh chapter derives the basic equations of the theory which describe the so-called ionic atmosphere and the time of relaxation of this atmosphere.

The next chapter is devoted to the thermodynamic properties of solutions. The concept of the activity coefficient which was originally developed empirically as a measure of the deviation of real solutions from the hypothetical ideal solutions is given a firm theoretical basis and applied to the colligative properties of solutions and to the influence of added electrolytes on the dissociation of weak acids (neutral salt effect) and on the solubility of other salts or non-electrolytes (solubility product law and salting out effects). The heats of dilution of solutions are also discussed in this chapter.

The ninth chapter is devoted to the electric conductance of solutions––a field in which the new theory has led to important advances because the Debye point of view differs so fundamentally from that of Arrhenius. The square root law for the variation of the conductance of extremely dilute solutions with the concentration which was long ago discovered empirically by Kohlrausch has been derived theoretically by Debye and later in an improved manner by Onsager. Debye and Falkenhagen have predicted that at very high frequencies the conductivity would depend on the frequency and this prediction has been verified experimentally after it was made. Finally Wien's experimental demonstration that Ohm's law fails at very high voltages has been shown to be a consequence of the new theory.

The tenth chapter is devoted to the viscosity of solutions—a field in which the theoretical development is due chiefly to Falkenhagen.

The greatest weakness of the Debye theory in the early stages of its development was that the mathematical difficulties of a rigid development compelled the introduction of inexact assumptions for the sake of simplification and as a consequence the resulting equations were only valid for extremely dilute solutions. The eleventh chapter shows substantial and encouraging progress in conquering these difficulties. The attempts to distinguish between the dissociated and undissociated fraction of the electrolyte by optical means (absorption spectra, refractive index, Raman effect) are discussed. The work ends with an account of the application of statistical methods to the problem by Fowler and by Kramers.

The title "Elektrolyte" may be misleading as it tends to give the impression that the work is a comprehensive discussion of all properties of solutions, whereas some properties of solutions, such as the compressibility, the coefficient of expansion, and diffusion coefficients, which have not yet been interpreted by the new theory are not discussed. It is, however, surprising that a discussion of transference numbers is omitted. One of the outstanding weaknesses of the Arrhenius theory is that it predicts that transference numbers should be independent of the concentration whereas it has long been known that in general transference numbers do vary with the concentration and this is an obvious corollary of the new theory of conductance and therefore would seem to merit comment in this book.

Citations to the original literature are of course given abundantly in the footnotes but the author relegates too much important and interesting discussion to the footnotes, which are printed in such small type that many users of the book will be unable to read the footnotes without eyestrain. Thus for example Bronsted's interesting views as to the nature of acids and bases and as to the mechanism of acid and base catalysis are discussed in a footnote which extends over three pages.

However, these criticisms concern minor matters. The book as a whole gives an admirable, systematic and substantially complete presentation of the new interionic attraction theory as developed up to the early part of 1932. It will be extremely helpful to anyone who wishes to acquire a really up-to-date knowledge of electrochemistry. It will be indispensable to research workers in this field and will unquestionably catalyze further development of our knowledge of solutions.

GRINNELL JONES

Applied **X-Rays**. By GEORGE L. CLARK, PH.D., Professor of Chemistry, University of Illinois. Second edition. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, 1932. xiv + 470 pp. Illustrated. 15 X 23.5 cm. Price, $5.00.

The second edition of Applied X-Rays has been largely rewritten and expanded to nearly twice the size of the first edition. The general scope of the book has remained the same, although much new material has been included. As the author states in the first edition, "the book aims to tell what this new tool is, how it may be used, what results it produces, why it can be applied to practical problems of everyday life, and how industry is beginning to use it.'"

Part I comprises properties of x-rays, x-ray equipment, spectra, chemical analysis from x-ray spectra, absorption and scattering, radiograph , and the physical, chemical and biological effects of x-rays. Part II is devoted to the x-ray analysis of the ultimate structure of materials. It includes crystals and x-ray diffraction, experimental methods, interpretation of diffraction patterns, results of crystal analysis for elements and inorganic compounds, crystal chemistry, structure of alloys, crystal structure of carbon compounds and several specialized subjects such as grain size and orientation, applications to metallurgical problems, colloidal and amorphous materials, liquids and polymerized organic substances

Part II contains a wealth of diverse material much of which is not to be found except scattered through the various journals. Throughout the book the treatment is descriptive and suggestive rather than detailed or theoretical. For example, the lay reader is given a rather clear idea as to how the structure of crystalline materials is worked out but in a general way not in detail. However, for the large group of readers who are more interested in knowing how x-rays can be used in various problems and what results have been obtained by their use, this book will be of the greatest value. To this large group of readers the book is to be highly recommended.

BERTRAM E. WARREN

Methoden der **Kristallstrukturbestimmung** mit **Röntgenstrahlen.** I Bd. Die Lauemethode. (Methods for the Determination of the Structure of **Crystals** by Means of Rontgen Rays. Vol. I. The Laue Method.) By Dr. E. SCHIEBOLD, Professor at the University of Leipzig. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse **6,** Leipzig C **1,** Germany, **1932.** xii + **173** pp. **63** figs. **16.5** × **24.5** cm. Price, **M. 12;** cardboard cover, **M. 13.**

The Laue method is the first of **a** series of three monographs on the methods of crystal structure determination by x-rays. Vol. II, "The Rotating Crystal Method" is now in press, and Vol. III, "Debye-Scherrer and Powder Method," is in preparation.

The Laue method was chosen as the subject of the first volume of this series as being the original diffraction method. The author's long years of experience with this method and its practical application to crystal structure determination make him well qualified to write this monograph. The subject matter includes the experimental technique of the Laue method, the indexing of Laue patterns by analytical and graphical methods, crystal symmetry, determination of the lattice constants, the Bravais lattice. space groups, intensity of the diffraction spots, arrangement within the unit cell and parameter determination. Chapter V on the intensity of the diffraction spots contains 56 pages and comprises a rather complete summary of the more important factors which enter this phase of the problem.

It is strange that although the graphical method of the gnomonic projection is in practice the simplest method of indexing Laue patterns, and almost exclusively the method used in this country, the author should have passed over this subject in a few pages and devoted **24** pages to the indexing by analytical methods. **Actually** this is probably a good point, in that one has here what is not generally found in discussions of the Laue method, and furthermore one glance at the 24 pages of wearisome trigonometric equations and laborious analytical calculations is the most convincing way of deciding that the graphical method justly deserves the popularity which it **has** always enjoyed in this country. Vector notation is used **very** little and the non-mathematically minded reader will have no trouble.

The paper and binding are good and the printing and reproductions clear, but in the copy reviewed the printing rubbed rather badly under finger touch.

BERTRAM E. WARREN

The Catalytic Oxidation of Organic Compounds in **the** Vapor **Phase.** By L. F. MAREK, Massachusetts Institute of Technology, and DOROTHY A. HAHN, Ph.D., Mount Holyoke College. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1932. 486 pp. 60 figs. 16 X 23.5 cm. Price, $9.00.

The great industrial importance of organic gas-phase oxidation processes has resulted in the recent accumulation of a vast amount of more or less empirical data, much of which is hidden in the patent literature and in obscure technological publications. At the same time, there has been a marked development in the theoretical viewpoint of the nature of contact catalysis, and the concept of chain reactions has been applied to gas-phase oxidations with significant results.

However, there has been no adequate review of this field as a whole since the books, published ten or more years ago, by Rideal and Taylor, Sabatier and Reid and Falk. In supplying this deficiency, "it has been the purpose of the authors to consider the facts regarding both developed and undeveloped processes and to review these critically in so far as possible."

The result, this present volume, contains a complete survey of the general literature, an excellent critical selection of patents, and numerous valuable private communications: a total of nearly 2000 references. All organic gas-phase oxidations, whether known to be catalytic or not, have, quite sensibly, been considered; moreover, much relevant information on liquid-phase oxidations is included. In addition, many closely associated parallel reactions such as dissociation, polymerization, hydration, etc., are reviewed in order to complete the picture.

Thus, a chapter on the thermal decomposition of ethyl and the higher alcohols precedes one on their oxidation, and a complete review of the reactions of the water gas system introduces a study of the oxidation of methanol to formaldehyde. The paraffins from methane to pentane are of particular interest owing to "the tremendous possibilities offered for conversion to valuable chemicals," and their oxidation is considered in detail. Other chapters deal specifically with the production of hydrogen from methane, and with surface combustion. The oxidation and hydration of the lower olefins and acetylene are reviewed together. A chapter on the oxidation of petroleum oils deals with the aliphatic hydrocarbons heavier than pentane. Additional data on the members of the gasoline range, together with reviews of ignition temperatures, oxidation mechanism and inhibition (for which the authors continue, at times, the use of the unfortunate term "negative catalysis") are found in a special section, "The Cause and Suppression of Knocking in Internal Combustion Engines." Aromatic compounds are reviewed in three chapters, devoted principally to the oxidation of benzene and naphthalene. Finally, there is a discussion of the apparatus used in commercial processes. Throughout these chapters the authors have by no means restricted the citations to work dealing specifically with the subjects in question, but have included numerous references to matters of allied interest.

A general description of the characteristics of gas-phase catalysis and its theoretical background is given in a brief introductory chapter. Further references to theory are found at intervals throughout the book, but'on the whole the treatment of this aspect has been subordinated to the presentation of practical or experimental facts. The authors acknowledge that "In many cases, the discussion could not be made as critical as desired, because of trade secrecy..., the multiplicity of conditions used..., and the paucity of data."

The immense amount of diverse material covered necessarily entails a certain degree of confusion in its presentation, which in this case is augmented by the fact that the chapter headings in the Table of Contents have not been subtitled, as is customary in these Monographs and as was done so effectively in the classic treatise of Sabatier and Reid. Moreover, there are no author and patent indexes.

In spite of these deficiencies, this volume undoubtedly constitutes a valuable reference work, complete and up-to-date As a time-saving source-book alone, it may well be worth many times its high price.

HAROLD A. BEATTY

Applied Colloid Chemistry. General Theory. By WILDER D. BANCROFT, World War Memorial Professor of Physical Chemistry at Cornell University. Third edition. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, 1932. ix + 544 pp. Illustrated. 14.5 × 21 cm. Price, $4.00.

Bancroft's third edition of Applied Colloid Chemistry is the "Golden Bough" of the subject and Bancroft is its Frazer. He has brought the book up to date in countless details and added over 10% to the pages of the second edition (1926). Everything which is even remotely connected with the colloid state is given at least a brief reference and some things which are not. The original 60 things which he said one can only know about after understanding colloids, have had one change (pharmacy becomes pharmacology); one addition, medicine, and one apparent addition, for "it now looks as though insanity were primarily a problem in colloid chemistry."

The book is interesting because it makes such an enormous number of natural phenomena seem more or less interrelated and within the colloid family. Everyone who wants to study colloidal chemistry thoroughly ought to possess it. The author probably reads more widely in chemistry than any other person who also writes, and he adds a great deal to his subject through his own experiments and those of his students. He is neither dogmatic nor captious but rather eclectic, and the book contains more references to the literature than any other book I have read. The data on "Thickness of Surface Films" (chapter XVII) have been about doubled.

W. R. WHITNEY

The Free Energies of Some Organic Compounds. By GEORGE SUTTON PARKS, Associate Professor of Chemistry, Stanford University, and HUGH MARTIN HUFFMAN, Assistant Professor of Biochemistry, California Institute of Technology. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1932. 251 pp. Illustrated. 15.5 × 23.5 cm. Price, $4.50.

In this book the authors have given a complete and fairly detailed account of the measurements that have been made on the free energies of organic compounds. This alone would make the book a valuable contribution to chemical literature, but they have enhanced its importance by including a system whereby the free energies in the liquid state of most of the simpler types of organic compounds can be calculated from their structures. Even for so complicated a substance as mannitol the calculated and observed values differ by only 1500 calories. When, as in eicosane, the calculated values differ by more than 10,000 calories the authors boldly claim the greater accuracy for the calculated value. The reviewer believes that future experiments will confirm the authors' conclusion.

The free energy increment per methylene group for gaseous olefins is less than the common value for liquid paraffins and liquid fatty acids. This result appears improbable, as the free energy increment per methylene group should be greater in the gaseous than in the liquid state. The increment for the olefins may easily be in error, for it is calculated from the free energy difference between the first and fifth members of the series. This difference is too small for accuracy. Further, the calculation of the free energy increment per methylene group should not involve the first member of a series, for first members often have anomalously high free energies.

The American Chemical Society is to be congratulated on this valuable and interesting addition to its monographs.

GERALD BRANCH

Jahrbuch der **organischen Chemie.** (Yearbook of **Organic** Chemistry.) By Professor Dr. JULIUS SCHMIDT, Stuttgart. Vol. XVIII, 1931. Verlag von Franz Deuticke, Helferstorferstrasse 4, Wien, Austria, 1932. xix + 345 pp. 17.5 X 25.5 cm. Price, M. 36; bound, M. 39.

The Jahrbuch has attained maturity. In celebration of the twenty-fifth anniversary of the first issue, Professor Schmidt has added to the present volume a foreword in which he reviews his struggle to keep the series alive despite war and depression, and expresses his joy and pride in its final success. The pride is justifiable; the author can be congratulated whole-heartedly on his achievement. He has steadily reported in his Jahrbuch all researches in organic chemistry that were manifestly significant, and year by year his reports have followed the trends of the investigators, faithfully reflecting the great interest in natural products and in the application of new physical methods The latest volume is the best of the series.

E. P. KOHLER

Qualitative Organic Analysis. An Elementary Course in the Identification of Organic Compounds. By OLIVER KAMM, Scientific Director, Parke, Davis and Company. Second edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. ix + 311 pp. 15.5 X 23.5 cm. Price, $2.75.

The second edition of this well-known textbook should be most welcome, not only to those already familiar with the earlier issue, but also to all organic chemists who wish up-to-date information in this fundamentally important field.

The general outline, arrangement of the material and method of presentation remain practically the same as in the first edition, the book being divided into a Theoretical Part (A), Laboratory Directions (B) and Classified Tables of Compounds (C). A subject index concludes the book. On the inside of the back cover is pasted a Solubility Table showing just how solubilities are used as the basis for the primary division of organic compounds into main groups.

The systematic procedure in the identification of an unknown remains as before, namely: 1, physical examination; 2, a determination of constants; 3, elementary analysis; 4, solubility tests; 5, determination of homologous series; 6, consultation of literature, tables, etc.; and 7, preparation and identification of derivatives.

Like most of the Wiley publications, type and paper are excellent, the proof-reading has been well done, and the few typographical errors noted are not serious.

The following comments are offered: (1) *Amide Formation* (pages 60, 186, etc.).—The student should be cautioned not to pour a large amount of concentrated ammonium hydroxide solution upon a liquid ester (for example, ethyl oxalate) in a test-tube, for the violence of the reaction may hurl the material into his face. (2) *Coupling of Heterocycles* (page 73).—While it is true that the nitrogen heterocycles themselves do not ordinarily couple with diazonium salts, this is not the case with all of their derivatives, many of which (notably the hydroxyl derivatives) yield dyes which have been patented. (3) *Diarylhydrazines* (page 73).—The difference in basicity and in other properties between the *sym.* and the *asym.* diphenylhydrazines should be pointed out, because the latter are used subsequently in certain reactions. (4) *Proteins* (page 97).—The xanthoprotein reaction is described as "a common test for the *phenolic* group." *(5) 1,2-Diketones* (page 108).—The inclusion of the quinoxaline (or phenazine) reaction is recommended as a test for these diketones, since this condensation generally occurs instantaneously and quantitatively in alcoholic solution with o-phenylenediamine, the products are crystalline, easily purified and of sharp melting point. It is generally simpler and much more satisfactory than the benzilic acid rearrangement, and is, of course, equally useful in the identification of 1,2-diamines.

MARSTON TAYLOR BOGERT

Aluminiumchlorid in der organischen Chemie. (Aluminum Chloride in Organic Chemistry.) By GEORG KRÄNZLEIN, I. G. Farbenindustrie A.-G., Höchst am Main. Second, revised and enlarged edition. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 143 pp. 16 X 23.5 cm. Price, Mk. 12.

In this handy volume the author presents an excellent picture of the role of aluminum chloride in organic chemistry—its service in synthesis; its action in reactions which involve reduction, dehydrogenation, rearrangement, polymerization or cleavage; and its technical applications. The various modes of action are illustrated with carefully selected examples, and supported with very many references to the literature.

Monographs on special topics in organic chemistry are becoming increasingly valuable both to the student and to the investigator. This volume on an important reagent is one of the best of its kind.

E. P. KOHLER

The Terpenes. Vol. II. The Dicyclic Terpenes, Sesquiterpenes and their Derivatives. By J. L. SIMONSEN, D.Sc. (Manc.), F.I.C., F.R.S., Proiessor of Chemistry, University College of North Wales. The Macmillan Company, 60 Fifth Ave., New York, 1932. xi + 627 pp. 14 × 22.5 cm. Price, $7.00.

With the publication of the second volume of "The Terpenes" the author has given us a work which will be indispensable to the student of terpene chemistry. As stated in the preface, few, if any, natural products have formed the subject of such intensive study as the pinenes and camphor. The section dealing with the sesquiterpenes includes the brilliant researches of Ruzicka and his collaborators.

The present work is more than a mere review of the literature, and could only have been written by one thoroughly acquainted with the subject. The development of the views regarding chemical constitution is taken up in order, and where further research is needed, the author has so indicated.

It is gratifying to have so excellent a work on the terpenes available in the English language.

E. K. NELSON

BOOKS RECEIVED

January 15, 1933–February 15, 1933

KURT **ALDER.** "Die Methoden der Dien-Synthese." Handbuch der biologischen Arbeitsmethoden, Emil Abderhalden, Editor. Abt. I, Chemische Methoden, Teil 2, 2 Hälfte, Heft 9 (Schluss). Urban and Schwarzenberg, Friedrichstrasse 105 B, Berlin N 24, Germany. 212 pp. RM. 13.50.

HANS **BODE** AND HANS **LUDWIG.** "Experimentelle Einführung in das Wesen organisch-chemischen Reaktionen insbesondere fur Lehramtskandidaten." Verlag Franz Deuticke, Helferstorferstrasse 4, Wien, Austria. 48 pp. M. 1.50.

GUSTAV BONWITT. "Das Celluloid und seine Ersatzstoffe. Handbuch für Herstellung und Verarbeitung von Celluloid und seinen Ersatzstoffen." Union Deutsche Verlagsgesellschaft Zweigniederlassung Berlin, Kraussenstrasse 35–36, Berlin SW 19, Germany. 813 pp. RM. 85.

C. DRUCKER and E. PROSKAUER, Editors. "Physikalisch-chemisches Taschenbuch." Vol. II. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6. Leipzig C 1, Germany. 481 pp. M. 15; bound, M. 17.

ANDRÉ GEORGE. "Mécanique Quantique et Causalité." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris Ve, France. 18 pp. Fr. 6.

FRANZ HOLZL. "Anleitung zur Massanalyse. Eine Einführung in die Elemente der Theorie und in das praktische Arbeiten für Studierende der Chemie und Pharmazie." Verlag von Franz Deuticke, Helferstorferstrasse 4, Wien, Austria. 141 pp. M. 4.

M. NIERENSTEIN. "Incunabula of Tannin Chemistry." A Collection of Some Early Tapers on the Chemistry of the Tannins. Reproduced in Facsimile and Published with Annotations. Edward Arnold and Co., 41-43 Maddox St., London W 1, England. 167 pp. 12 s./6 d. net.

F. F. NORD and R. WEIDENHAGEN. "Ergebnisse der Enzymforschung." Band II. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C1, Germany. 358 pp. M. 28; bound, M. 30.

FENTON B. TURCK. "The Action of the Living Cell. Experimental Researches in Biology." The Macmillan Company, 60 Fifth Ave., New York. 308 pp. $3.50.

J. H. WHITE. "The History of the Phlogiston Theory." Edward Arnold and Co., 41-43 Maddox St., London W 1, England. 192 pp. 6 s., net.

"Annual Tables of Constants and Numerical Data, Chemical, Physical, Biological and Technological." Published under the Patronage of the International Research Council and of the International Union of Chemistry. McGraw-Hill Book Co., Inc., 330 West 42d St., New York. Vol. VIII, 2 parts (1927–1928), 2706 pp., $20.00. Vol. IX (1929), 1607 pp.; Index to Vol. IX, 124 pp.; $16.00.

"Gmelins Handbuch der anorganischen Chemie." 8 Aufl. System-Nummer 30, Barium. Herausgegeben von der Deutschen Chemischen Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 390 pp. Mk. 56 to subscribers; Mk. 64 separately

"Micro Chemistry at New York University." New York University Centennial. Band XI, Lieferung 2, Neue Folge, Band V, *Mikrochemie*. Emil Haun and Co., Maria-Theresien-Strasse, Wien I, Austria 368 pp.

"An Outline of Atomic Physics." By Members of the Physics Staff of the University of Pittsburgh. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 348 pp. $3.50.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

The Quantitative Determination of Palladium by Means of Ethylene[1]

BY S. C. OGBURN, JR., AND W. C. BRASTOW

Of the six platinum metals, palladium is the most readily reactive with organic reagents with the formation of stable coordinated salts.[2] The use of these compounds, however, for the quantitative estimation of palladium, or its removal from the other metals of the group, necessitates the use of a gravimetric factor to convert the weighed precipitate to percentage of the metal present. If the metal itself is desired, the precipitate must be reduced by ignition in a stream of hydrogen. Certain reducing agents as powdered zinc or magnesium, formic acid, hydroxylamine, phenylhydrazine and others can be used to yield the metal directly from acid solutions of the metallic chloride, but in these cases platinum, if present, and usually others of the group are also precipitated.

It appears desirable, therefore, to be able to select some reducing agent which is selective in its action and which offers no particular disadvantages in the analytical procedure for the removal of palladium in the metallic condition from a mixture of the platinum metals group. Carbon monoxide acts in this capacity when introduced into strongly acid solution of the chloride of the metals[3] but offers the disadvantages of slowly reducing platinum and of tending to convert the other metals present into ionic complexes from which they are, subsequently, not easily precipitated. Of the simple unsaturated hydrocarbon gases, acetylene forms a reddish-brown precipitate which yields the metal on heating.* It also has a tendency to reduce slowly other metals of the group, yielding an undesirable colloidal condition.[2] Ethylene, however, seems to be admirably adapted to meet the needs of this problem. It is specific in its reduction of palladium with respect to the others of the group; it is cheap and easily obtainable in compressed form; and it offers a means of separating, quantitatively, large

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(1) This paper is taken, in part, from a thesis submitted by W. C. Brastow to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Bachelor of Science.

(2) Ogburn, THIS JOURNAL, 48, 2493 (1926).

(3) Manchot, *Ber.*, 58B, 2518 (1925).

(4) Erdmann and Makowaka, *ibid.*, 37, 2694 (1904).

amounts of the metal which would be of value industrially as well as analytically.

Experimental Part

Preparation of **Solutions.**—In order to increase the range of accuracy of the analytical methods used to standardize the palladium chloride solutions, two were prepared. The one was obtained by dissolving the pure salt, $PdCl_2 \cdot 2H_2O$, in hot water containing about 7 cc. of concentrated hydrochloric acid per 100 cc. of solution, and filtering. The other was made by dissolving a weighed quantity of pure palladium wire in aqua regia. After carefully evaporating this solution to dryness on a water-bath, the residue was taken up with concentrated hydrochloric acid and the whole reevaporated until nitrogen oxides ceased to be evolved. The evaporation to dryness was repeated and a second addition of the acid was made after which it was diluted to the same acid concentration as in the preceding case.

The solutions of ruthenium trichloride, sodium chlororhodite, potassium chloroosmate, sodium chloroiridate and chloroplatinic acid were prepared according to directions given by one of us.[2] The metallic contents of these were determined by reduction with zinc, followed by ignition in a stream of hydrogen, with the exception of the osmium solution, which was immediately filtered into a weighed Gooch crucible, washed and dried at 105".

The metallic content of the palladium chloride solution obtained from the solution of the salt was determined by means of precipitation with dimethylglyoxime and the use of the proper gravimetric factor.

The ethylene gas used was from a cylinder as purchased in a purified form from one of the commercial producers.[5] The manufacturers' analysis as given in a private communication was: ethylene 99%; air 1%.

Standardization Results.—Ten-cc. samples of the solutions were used for each determination. At least four analyses were made with each. The maximum, minimum and mean values obtained are as follows (expressed in grams of the metal per cc. of solution):

	Maximum	Minimum	Mean
Palladium	0.02160	0.02148	0.021501
(From the salt, $PdCl_2 \cdot 2H_2O$)(Dimethylglyoxime as the reagent)			
Palladium			.019994
(From metallic wire) (Solution made from weighed sample)			
Rhodium	.0027	.0025	.002625
Ruthenium	.0032	.0030	.003125
Osmium	.0030	.0026	.002755
Iridium	.0028	.0027	.002770
Platinum	.0024	.0021	.002230

The Removal of Palladium from a Solution of Palladium Chloride.—Before attempting the separation of the palladium from all of the platinum metals in a mixture, by means of ethylene, the procedure developed was carried out with a solution of the palladium chloride alone, and was done as follows. A ten-cc. portion of the solution was heated on a water-bath to 80°. Ethylene gas was rapidly passed in until reduction was complete and the precipitate had coagulated to leave the supernatant liquid clear and colorless. After settling, the mixture was filtered through a properly prepared Gooch crucible. The precipitate was washed with warm water until the washings were free from chlorides, and then dried in an electric oven at 105° to a constant weight. A test of the filtrate with dimethylglyoxime solution showed the absence of any palladium.

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(5) The Matheson Co., North Bergen, N. J.

During the precipitation, the color of the solution is more quickly removed, and the colloidal condition of the finely divided metal easily overcome, if agitation is effected by means of a small motor-driven stirrer. Two hours is usually required to effect the complete reduction.

Varying temperatures, up to the boiling temperatute of the solution, and varying acid concentrations equivalent to from 5 to 20 cc. of concentrated hydrochloric acid per 100 cc. of solution were tried in an effort to ascertain any differences either in the rate of the reduction or its completeness. No differences were noted, except that at the lower temperatures the process of removal of the metal was appreciably retarded. With more concentrated solutions of the metal, the reduction appears to be more rapid.

In order to verify the fact that the black spongy precipitate was metallic palladium and not an organic derivative, separate determinations were made and weights taken before and after reduction in hydrogen for twenty minutes at red heat. No change in weight resulted, and in each case the percentage of the palladium checked with the quantity in the original sample, within the range of experimental error. Five analyses, each made in duplicate, gave maximum, minimum and mean values of grams of metal per cc. as follows.

Solution 1. (Palladium chloride prepared from the pure salt, $PdCl_2 \cdot 2H_2O$.)
Maximum, 0.02180 Minimum, 0.02140 Mean, 0.021683.
Theoretical value (as determined from dimethylglyoxime determination) 0.021501.
Error, +0.846%.

Solution 2. (Palladium chloride prepared from pure palladium wire.)
Maximum, 0.01998 Minimum, 0.01990 Mean, 0.019955.
Theoretical value (as determined from weighed sample), 0.019994.
Error, −0.195%.

From these results, it may be readily seen that ethylene may be used to quantitatively remove palladium from its chloride solution.

The Removal of Palladium in the Presence of All the Platinum Metals.—In order to verify the accuracy of the separation of palladium from all of the other metals of the platinum group, a mixture of solutions of each of the six metals of the concentration previously mentioned was prepared. Each 100 cc. of this solution contained the following.

	Grams	Metal %
Platinum	0.0669	18.38
Palladium	.19994	54.94
Iridium	.0277	7.61
Osmium	.0275	7.56
Rhodium	.02625	7.21
Ruthenium	.015625	4.29
Total metal content	0.363915	99.99

The reason for using an excessive amount of platinum was that it is the principal metal found associated with palladium, both in nature and in industrial materials.

The removal of the palladium by means of ethylene was made as before. The maximum, minimum and mean values for the recovered metal from three determinations, in which 100-cc. samples of the solution mixture were used, ran as follows (expressed in terms of grams of palladium recovered from each sample):

Maximum, 0.2015 Minimum, 0.1961 Mean, 0.19845
Theoretical value, 0 19994 Error, −0.746%.

In order to determine whether the palladium was contaminated with other metals of the group, the combined precipitates were dissolved in hot dilute aqua regia (in which they were completely soluble). After evaporation nearly to dryness concentrated hydrochloric acid was added to facilitate the removal of nitrogen oxides. The evaporation to dryness was repeated and the residue taken up with water containing a small amount of hydrochloric acid. Upon analyzing this solution according to the method described in a previous paper[6] it was found that no weighable amount of metals other than palladium was present. A small amount of platinum was indicated by a slight color reaction with potassium iodide and also with α-furil dioxime, but the latter did not yield a precipitate sufficient to weigh within any degree of accuracy.

It may be thus seen that the presence of the other metals of the group has but slight effect in the removal of the palladium. The percentage error shown is low in comparison with standard procedures used to effect this task. At best the analytical separations of the platinum metals are not usually as conclusive as those available for use with others so widely known. A means, therefore, which can be attained quickly to yield the metal directly is desirable. The selective action of ethylene also adds to this advantage.

Summary

A new and practical method for the determination of palladium, either alone or in mixtures of all of the other metals of the platinum group, is given. By means of the specific action of ethylene gas toward palladium in reducing it to the metallic condition, gravimetric factors need not be used, and the process of reduction of organic derivatives of the metal in hydrogen is not necessary, when the metal is desired as an end-product. In mixtures of the six platinum metals, the error in the recovery of the palladium is only about 0.75%.

[6] Ogburn, THIS JOURNAL, 48, 2507 (1926).

LEWISBURG, PENNSYLVANIA

RECEIVED JULY 1, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Use of the Tungsten–Nickel Electrode System in Neutralizations[1]

BY N. HOWELL FURMAN AND GEORGE W. LOW, JR.

This investigation of the bimetallic electrode system, tungsten–nickel, was made in order to determine the possibilities of the system in neutralizations. Kahlenberg and Krueger[2] were the first to make a comprehensive study of the use of bimetallic systems in neutralizations. They used normal solutions of strong acid and base, and recommended especially tungsten in conjunction with one of the following: copper, nickel, silicon or cobalt. They gave no data for weak acids or bases. In a subsequent paper Holt and Kahlenberg[3] studied various systems in greater detail, using 0.1 *N* solution of hydrochloric acid, sodium hydroxide, ammonium

[1] Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

[2] Kahlenberg and Krueger, *Trans. Electrochem. Soc.*, 56, 201 (1929).

[3] Holt and Kahlenberg, *ibid.*, 67,361 (1930).

hydroxide and various amines. They stated that the nickel electrode is unsatisfactory because it is attacked by acids. In our work this difficulty did not prove to be serious. They added the reagent in increments of 0.2 cc., which makes it difficult to judge whether a particular electrode system is of value for precise work.

Various bimetallic systems have been studied by other investigators. Willard and Fenwick[4] found that the polarized platinum system gave a good indication of the end-point in the titration of a strong acid with a strong base. Brünnich[5] stated that the system platinum–graphite gave satisfactory results in the titration of both weak and strong acids with sodium hydroxide. Fuoss[6] recommended the following pairs of electrodes for neutralizations: Sb–Pb, Bi–Ag, Sb–Cu amalgam, Cu–CuO.

None of these investigators checked the potentials of the two metals repeatedly against a reference half cell as has been done in this work. Closs and Kahlenberg,[7] however, determined end-points with systems composed of a single metal and a calomel electrode. They found tungsten, bismuth, arsenic, antimony and molybdenum to be the best indicator electrodes.

Experimental

Materials and Apparatus.—Tungsten wire 0.635 mm. in diameter, and nickel wire 1.829 mm. in diameter were used. The surfaces of the electrodes were cleaned with emery paper and by treatment with nitric acid. A saturated calomel cell and a Leeds and Northrup students' type potentiometer and accessories were employed. Solutions were stirred with a motor-driven stirrer. The calibration of the volumetric ware was checked and buret corrections were applied.

Approximately 0.5 and 0.1 N solutions of the various reagents were prepared and standardized by well-established methods. The alkali solutions were nearly, but not entirely, freed from carbonate and protected by "ascarite" tubes.

During titrations at least three e. m. f. readings were taken after additions of reagent, namely, tungsten–nickel; tungsten-calomel; nickel-calomel. The electrical end-points (maxima of Δ e. m. f./Δ cc.) were compared with the end-points obtained in independent titrations using phenolphthalein or methyl orange indicators. The presence of a small amount of carbonate in the alkali caused two electrical end-points to be found, one at the end of the neutralization of free alkali and conversion of carbonate to bicarbonate, and the other at the end of reaction between bicarbonate and acid.

A summary of typical data is given in Table I.

When alkali was titrated with acid, carbon dioxide was absorbed from the atmosphere, and hence the phenolphthalein end-point was determined either by having the indicator present during the titration, or by independent titrations run under similar conditions.

The titration of a strong acid with a strong base or *vice versa* is satisfactory either in 0.5 N or 0.1 *N* solution. A careful study of the e. m. f.-cc. graphs for the individual metals against the calomel electrode made it

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(4) Willard and Fenwick, This Journal, 45, 715 (1923).

(5) Brünnich, *Ind. Eng. Chem.*, 17, 631 (1925).

(6) Fuoss, *Ind. Eng. Chem., Anal. Ed.*, 1, 125 (1929).

(7) Closs and Kahlenberg, *Trans. Electrochem. Soc.*, 54, 369 (1928).

TABLE I

END-POINTS

Solution in beaker (approx normality)	Size of sample, cc.	Solution added (approx. normality)	Phenolphthalein		Methyl orange	
			Indicator, cc	Electrical, No. 1	Indicator, cc.	Electrical, No 2
0.5 *N* NaOH	25.02	0.5 *N* HCl	17.27"	17.15	1762	17.65
	25.02		17.42"	17.42	17 62	17.63
	9.97		6.77	6.77	7.07	7.04
	9 97		6.82	6.78	7.02	7.02
	9 97				7 02	7 02
0 1 *N* NaOH	24.93	0 1 N HCl	17 26	17.16	18 41	18 48
	9.99		693	693	7.53	7.46
	9 99		6.98	7.02	7.45	7.45
0 5 *N* HCl	25.03	0.5 *N* NaOH	3538	3538	3528	35.30
	25 03		35 43	35.43	35.33	35.33
	10 03		1414	1409	1399	14.03
	10 03		14.24	1419	14.14	14.14
0 1 N HCl	24 95	0 1 N NaOH	33.91	33.86	33.66	33.66
	24.95		3391	33.96	33.66	33.71
	9 97		13.47	13.42	13.29	13.33
0 2 *N* HAc	2000	0.5 *N* NaOH	11.10	10.93		
	20 00		11 07	10.91		
	10 00		5 68	5 48		
0 2 *N* HAc	10 00	0 1 N NaOH	27.12	25 58		
	5 00		13 53	12 38		
	5.00		13 58	12 48		
0.5 *N* NH$_4$OH	2000	0.5 *N* HCl			18 27	18.24
	10 00				918	9.14
	10.00				9 53	9 54 (CO$_2$)
Na$_2$CO$_3$	1 4753 g.	0 5 N HCl			55 14	55.10
	1 0969				40.96	40.94
	1.0665				39.86	39.82
	0.8995				33.54	33 56
0.5 *M* H$_3$PO$_4$	1000	0.5 *N* NaOH	No results which could be interpreted			

[a] The discrepancy between these values is due to different rates of titration, and very long exposure of the second solution to air. The second end-point is exact.

clear that the electrical end-point at the PH at which phenolphthalein changes was due primarily to the change in potential of the tungsten electrode, the nickel–calomel system being relatively insensitive in this region. The latter electrode system shows a large break in potential in the methyl orange region, and the change with reference to the calomel half-cell is in the opposite direction to that undergone by the tungsten (with reference to the calomel cell) in this region.

The titration of ammonia with hydrochloric acid gave excellent results, the break in potential (tungsten–nickel) being sharper than with the usual combination of indicator electrode and reference half-cell, because the rapid changes of the two metals are in opposite directions, as is shown in

Fig. 1 A and B. Study of a number of graphs not reproduced here indicates that the nickel electrode serves as an approximate *PH* indicator in alkaline solutions, for the graphs are nearly parallel to those given by the tungsten electrode. Near the end-point there is an abrupt discontinuity in the behavior of the nickel, and in the acid region the nickel-calomel system shows little tendency to follow *PH* changes in a regular fashion. Holt and Kahlenberg (Ref. **3,** Fig. 2) pointed out that nickel and cobalt differed from most of the other metals which they studied in manner of change of potential upon passing from acid to alkaline solution or *vice versa*

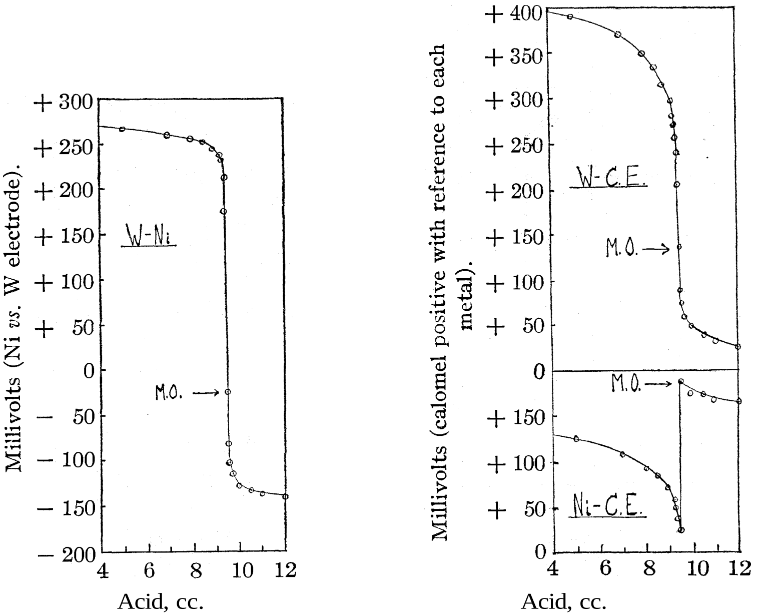

Fig. 1A. Fig. 1B.

Fig. 1.—A. Graph for titration of 10 cc. of approximately 0.5 N ammonia with 0.5 N hydrochloric acid, using the W-Ni system. B. Showing the behavior of the individual electrodes during the course of the titration represented in **A.** (M. O. indicates the methyl orange end-point. C. E. denotes the saturated calomel electrode.)

We should expect that the tendency of nickel to undergo a sharp change at a *PH* near the methyl orange transition (4–5), while exceedingly useful in the titration of weak bases, would vitiate the results in the titration of a weak acid with a strong base. This conclusion is amply borne out by the results in the case of acetic acid. As is shown in Fig. 2, A, B, there is an excellent electrical end-point in this titration, but the maximum change is always displaced from the true end-point though rarely or never to the same extent in successive titrations. There is a second small maximum in

A e. m. f./Δ cc. at the true end-point in the case shown in Fig. 2, but this maximum does not appear clearly in many of the titrations.

The erratic behavior of the nickel electrode was evident during the progress of titrations of sodium carbonate with hydrochloric acid. In some instances the minor electrical end-point which apparently corresponded to the phenolphthalein end-point was displaced several cc. (10 cc. in one case) from the indicator change. The second and major electrical change, however, coincided quite accurately with the methyl orange end-point.

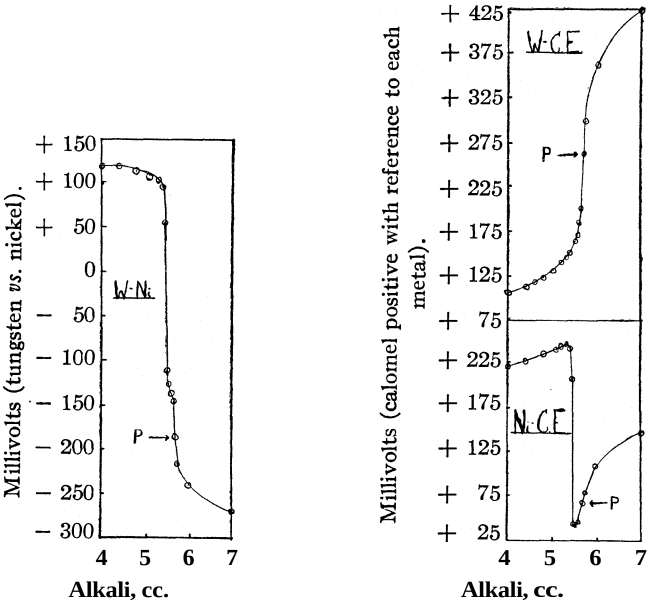

Fig. 2A. Fig. 2B.

Fig. 2.—A. A graph for titration of 10 cc. of approximately 0.2 N acetic acid with 0.5 N sodium hydroxide. P indicates the phenolphthalein end-point. B. Shows the behavior of the individual metals during the course of the titration plotted in A. Note the characteristic behavior of the nickel electrode.

It was not possible to interpret the results of the titration of phosphoric acid with alkali. Electrical maxima were obtained, but not at stoichiometric points. The largest jump in potential was observed when phenolphthalein was added after the first end-point, as indicated by the tungsten–calomel system, had been passed. In the presence of this indicator there were erratic potential changes *(nickel electrode)* during the titration of carbonate with acid.

Summary

The tungsten–nickel electrode system has been shown to be of value in the titration of strong acid with strong base, or *vice versa.*

The system appears to be one of the most satisfactory in the titration of weak base with strong acid. In the titration of weak acids or polybasic acids the system appears to be of little use.

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The Dependence of the Ultrafiltrate from a Sot of "Ferric Hydroxide" upon Rate of Ultrafiltration; Donnan Equilibrium and *PH* of Sols

BY JAMES W. MCBAIN AND WINIFRED L. MCCLATCHIE

The unequal distribution of all mobile ions in any system involving a restraint upon certain electrical charges, now commonly known as the Donnan equilibrium,[1] was given quantitative formulation in the subject of electrokinetics by Gouy and Chapman for the diffuse double layer in the neighborhood of surfaces and colloidal particles, then by Donnan in 1911 for membrane equilibria, and very much later by Debye and Hückel in 1923–1924 for the interior of ordinary solutions. Further, although the classical nomenclature of colloids, still frequently employed, took no cognizance thereof, it is well known that all charged colloids in ionizing solvents partake of the nature of salts.[2]

Nevertheless, these matters have been overlooked in assigning to hydrogen ion, or any other ion, definite values of concentration in a sol, although these must vary greatly according to the distance from a colloidal particle. It is intriguing to reflect that the readings of electrode potential of the hydrogen electrode (or other reversible electrode) in different parts of a sol must be identical, although the actual concentrations of any ion yielding the constant electrode potential must vary even as a time average from point to point. A portion of the liquid near a positively charged particle such as that in a sol of "ferric hydroxide"[3] must be less acid than that further away, and although exhibiting the same hydrogen or chloride electrode potential, the actual *PH* and P_{Cl} must be different in different parts of the sol. Serious discrepancies must, therefore, appear in the

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(1) For references, including the classical work of Gibbs, see T. R. Bolam, "The Donnan Equilibria," G. Bell and Sons, Ltd., London, 1932.

(2) For the most comprehensive and authoritative monograph, see Wo. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929.

(3) It should be recalled that a sol of so-called "ferric hydroxide" prepared from ferric chloride is a colloidal complex salt. It contains as essential constituents particles consisting of heavily hydrated oxide or hydroxide with undissociated oxychloride and the positively charged ferric or ferroxy ion, compensated by an electrochemically equal amount of free chlorine ions in the surrounding liquid. There is also a trace of hydrochloric acid in hydrolytic equilibrium. These sols are by no means necessarily dilute, they possess a moderate proper conductivity and definite lowering of freezing point, and they diffuse as rapidly as sucrose.

treatment hitherto accorded the study of the constitution of colloidal sols and even in most of the published values for P_H of colloids.

Ultrafiltration has frequently been employed as a tool in the study of colloids, yet there is only one paper, that of Greenberg and Greenberg,[4] in which the Donnan equilibrium is recognized and, even so, from the standpoint of membrane equilibrium rather than from the more general one outlined in these opening paragraphs, thus missing the main point of the present paper.

Most colloid chemists other than Pauli and his associates have assumed that an ultrafiltrate is identical with the solution in which the colloidal particles are suspended, quoting as evidence the observation of Duclaux,[5] Maffia,[6] and others (including Greenberg and Greenberg)[4] that the composition of the ultrafiltrate was independent of the amount filtered.

It has further been asserted by Kruyt, Roodvoets and van der Willigen[7] that the composition of the ultrafiltrate is independent of the density of the membrane, and in a recent paper by Duclaux and Titeica[8] that it is independent of the pressure applied. In other words, it is claimed that the composition of the ultrafiltrate is not affected by the rate of ultrafiltration. In neither case, however, are experimental data given for the composition of the sols or of the ultrafiltrates.

The series of ultrafiltrations to be described was incidental to the study of "sol 13" of "ferric hydroxide," the preparation and P_H of which were given in a previous communication.[9] It was especially desired to observe the effect of changing the pressure on the composition of the ultrafiltrate, for we have utilized a far wider range of pressures than those in previous work, namely, from less than one atmosphere up to one hundred atmospheres. We find that the concentration of the ultrafiltrate may be varied four-fold by mere change in the pressure or the rate employed, a phenomenon which has not been suspected by previous workers in this field.

Experimental

Ultrafiltration.—A high pressure ultrafilter,[10] equipped with an electrically operated stirrer, was used. All portions of the apparatus coming in contact with solution were heavily silver plated or were replaced by parts of pure silver, except for a nickel gauze underneath the membrane. All portions not of solid silver were coated with a thin

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(4) D. M Greenberg and M Greenberg, *J. Biol Chem* , *94*, 373 (1931). They found the concentration of salt in the ultrafiltrate to be greater than that in the original alkaline casein solution but independent of the amount filtered. Their reflection upon the interpretation of the ultrafiltration experiments of J. W. McBain and W. J. Jenkins [*J. Chem. Soc.*, **121**, 2325 (1922)] has been shown by subsequent work to be invalid.

(5) J. Duclanx, *Kolloid-Z.*, 3, 126 (1908).

(6) P. Maffia, *Kolloidchem. Beihefte*, 3, 85 (1911).

(7) H. R. Kruyt, A. C. W. Roodvoets, and P. C. van der Willigen, "Colloid Symposium Monograph," 1926, Vol. IV, p 304.

(8) J. Dnclaux and R. Titeica, *Compt. rend.*, 189, 101 (1929).

(9) W. L. McClatchie, J. *Phys. Chem.*, *36*, 2087 (1932).

(10) Vereinigung Gottinger Werke, Gottingen.

film of boiled out medicinal vaseline. Cellophanes "No. 600," "450" or "1200" were used for the ultrafilter membranes and all washers likewise were cut from cellophane "No. 2400," three or four thicknesses being required. All membranes and washers were soaked for at least twenty-four hours in several changes of conductivity water before being used. Pressure was applied from a cylinder of compressed nitrogen.

To test the apparatus for freedom from conducting impurities, conductivity water was filtered. It showed an increase in specific conductivity only of 0.5 to 1.0 $\times 10^{-6}$, which is well below the probable experimental error for the ultrafiltration of the sol.

The filter was rinsed with several portions of sol before the sample for ultrafiltration was introduced, and the first 10 to 15 cc. of ultrafiltrate was rejected, serving to saturate the membrane and to rinse the funnel below the filter. The sol was stirred at a moderate

TABLE I

THE EFFECT OF DIFFERENT PRESSURES USED IN ULTRAFILTRATION OF "FERRIC HYDROXIDE SOL 13" UPON THE COMPOSITION OF THE ULTRAFILTRATE

Expt	Cellophane No.	Portion	Press. kg/sq cm	Total % filtered	Rate[a] cc/min.	Ultrafiltrate $K \times 10^5$
1	600	2	40–50	20	0.21	6.97
		3	25–35	28	.32	6.42
		4	25–30	36	.28	6 42
		5	20–30	44	24	6 64
		6	30–60	55	.38	5 38
2	600	2	45–55	14	.39	5 01
	Same as	3	40-60	22	.38	4.99
	for No. 1	4	10–14	31	.17	8 68
		5		38	.18	9.07
		6	45–60	45	.40	4 52
3	600	2	90–100	15	.45	4.62
	New mem-	3	90	23	.42	4.90
	brane	4	52–55	33	.30	6 52
		5	50–52	39	.30	6 34
		6	6 7	47	.12	11 3
		7	6	53	.13	11.1
		8	95	64	.49	3.56
4	600	2	1–2	17	.12	13 6
	Same as	3	>1	27	.086	14 8
	for No. 3	4	50	43	.46	5 26
		5		54	.56	3.76
5[b]	450	3	46–50	47	.51	5 15
		4	60–65	54	.61	4 38
6	1200	2	5	18	.082	13.9
		3	3	21	.073	14.1
		4	50	27	.19	7.16
7	1200	2	1	23	.065	12.3
	Same as	3	>1	30	.061	12.4
	for No. 6	4		53	.11	8.32
8	600	3	13	23	.20	8.65
		4	6	35	.15	9.88
		5	65	47	.38	4 31

[a] The membrane area was about 28 sq. cm.

[b] Sol came through when pressure was first applied.

rate, and a current of air on the apparatus prevented heating by the electromagnets. The ultrafiltrate was collected in stoppered Jena or Pyrex containers. The results of these experiment.are collected in Table I. The last column gives the specific conductivity, at 25°, of the ultrafiltrate obtained.

It is obvious that the composition of the ultrafiltrate is by no means independent of the rate of ultrafiltration, and that it is the rate rather than the pressure that is the determining factor. This is shown by comparison of portion 2 of filtration 2 with portion 3 of filtration 3, where the pressures were different but the rates and conductivities were the same. The specific conductivities of the ultrafiltrates were, therefore, plotted against the rates of ultrafiltration, as shown in Fig. 1.

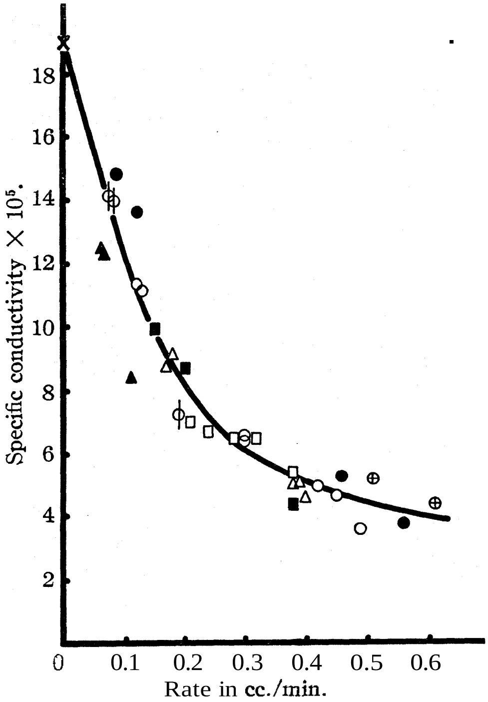

Fig. 1.—The effect of the rate of ultrafiltration of "ferric hydroxide" sol upon the composition of the ultrafiltrate: Expt. 1, □; Expt. 2, △; Expt. 3, ○; Expt. 4, ●; Expt. 5, ⊕; Expt. 6, ⏀; Expt. 7, ▲; Expt. 8, ■.

The general relationship between the rate of ultrafiltration and the conductivity is fairly well established by these experiments. The failure to obtain closer checks was probably due to temperature differences between the different samples that were ultrafiltered, as there is a tendency for all points from a single experiment to lie on the same side of the curve.

The main result cannot be attributed to any systematic influence of the amount filtered, or of the method of varying the pressure, or of temperature changes, for no routine method of varying the rates was followed. The frequently reported nearly constant composition of successive samples of ultrafiltrate is further confirmed by these experiments.

Dialysis.—It may be seen from Fig. 1 that the conductivity of the ultrafiltrate is still increasing rapidly at the lowest rates obtainable by ordinary ultrafiltration. It is of theoretical interest to know the limiting composition for zero rate or, in other words, after the residue and filtrate have come to an approximate equilibrium. Dialysis of the sol against its ultrafiltrate affords a means of evaluating approximately this equilibrium, although it is realized that the conditions obtained would not be quite identical with a zero rate ultrafiltration.

A 40-cc. sample of sol 13 was dialyzed at 25° against 50 cc. of ultrafiltrate with a specific conductivity of 6.4×10^{-5}. The sol was contained in a cellophane tube, and dialysis was carried out in a glass-stoppered conductivity cell of 150 cc. capacity.

TABLE II

Time in hours	0	$^3/_4$	$3^1/_2$	20	44	80
$K \times 10^5$ of dialyzate	6.4	11.8	16.4	14.7	19.0	19.0

The equilibrium concentration of the dialyzate, as shown in Table II, was plotted as point X in Fig. 1, and it fits fairly well on the curve for conductivity against rate of ultrafiltration.

Composition of the Ultrafiltrate.—The conductivity of the best conducting ultrafiltrate (lowest rate) is less than one-tenth of the total conductivity of the sol and it does not contain over one-twentieth of the total chloride. It contains the merest trace of iron, ammonium thiocyanate giving only a faint pink. Nessler's reagent indicated less than 10^{-5} N ammonia. Nevertheless, the conductivity of the ultrafiltrate was only partly due to free hydrochloric acid. This was shown by determining the concentration of hydrogen ion in the ultrafiltrate and in the dialyzate with a glass electrode[11] which had given concentrations of 1.2, 1.2 and 1.1 $\times 10^{-4}$ N with 1.0×10^{-4} N hydrochloric acid solution prepared by dilution of 1 N hydrochloric acid solution in two stages with boiled out conductivity water. The results are given in Table III. The next to the last column, headed C_{H^+} conductivity, is the concentration of hydrochloric acid that would be required to account for the total conductivity of the ultrafiltrate.

TABLE III

COMPARISON, USING GLASS ELECTRODE, OF CONDUCTIVITY OF ULTRAFILTRATE AND DIALYZATE WITH CONCENTRATION OF HYDROGEN ION PRESENT

Expt.	Portion	t°	"E"	"E_{KHP}"	$C_{\mathrm{H}^+} \times 10^5$	C_{H^+} cond. $\times 10^5$	$\frac{C_{\mathrm{H}^+}}{C_{\mathrm{H}^+}\text{ cond}}$
8	5	20	0.1175	0.0866	2.8	10.1	0.27
Not in Table I		24	.2260	.2335	7.9	18.0	.46
Not in Table I		24	.2280	.2335	8.7	18.0	
8	3	21	.1462	.1671	5.0	20.2	.25
8	4	20	.1512	.1671	5.8	23.2	.25
Dialyzate		19	.1675	.1627	16.0	46.3	.39
Dialyzate		19	.1718	.1625	20.0	46.3	

It is probable that there is a small concentration of some electrolyte derived from the glassware (or cellophane) to account for the greater portion of the conductivity of the ultrafiltrate. Fortunately, these concentrations are so low that they affect the total composition of the sol but little.

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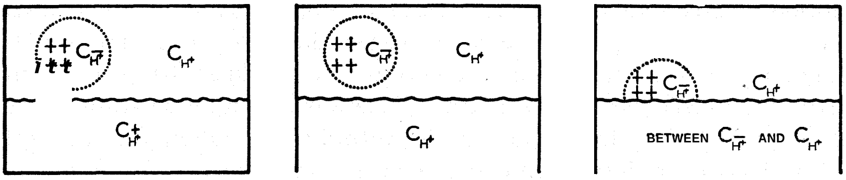
[11] For the technique and the reference electrodes and buffers, see W. L. McClatchie, J. *Phys. Chem.*, 36, 2087 (1932).

If the extrapolated value of specific conductivity of ultrafiltrate for highest rate be taken as 3.0 X 10^{-5} and it is assumed that 25% of this conductivity is due to hydrochloric acid and the remainder to some other chloride, the total chloride ion in the ultrafiltrate would be only 1.7 X 10^{-4} *N*. The chloride present in the original sol is, however, 0.04405 N, and nearly all of this, namely, 0.0439 *N* chloride, is an integral part of the colloid particles and their compensating ions. Similarly, of the total specific conductivity of the sol, 5.70 X 10^{-4}, 5.40 X 10^{-4} would be the proper conductivity of the colloidal particles and their opposite chlorine ions. In one liter of sol there were 0.912 gram equivalent of iron and 0.04405 gram equivalent of chlorine.

Discussion of Results

The conceptions arising in the present work are illustrated diagrammatically in Fig. 2. Here the membrane, impermeable to one colloidal species only, is represented by a wavy line. Dialysis or Donnan membrane equilibrium is regarded as the limit of slow ultrafiltration. For the sake of clarity only one colloidal particle is indicated by an aggregation of four adjacent positive charges and only the distribution of a single diffusible ion, in this case hydrogen ion, is indicated. The positive particle is surrounded by a domain influenced by its concentration of charges. Although this domain has no definite boundary and the influence falls off with distance according to the well-known exponential formula of Gouy, Chapman, Debye and Hückel, it is indicated for diagrammatic purposes by a dotted enclosure. There are thus three regions distinguished: first, that within the domain of the colloidal charges; second, the intermicellar liquid; and third, the dialyzate or ultrafiltrate.



(a) Dialysis or osmotic (membrane) equilibrium; infinitely slow ultrafiltration.

(b) Moderately slow ultrafiltration.

(c) Rapid ultrafiltration.

Fig. 2.—The effects of Donnan equilibrium within a colloidal sol or electrolyte upon the distribution of PH (or other ion) and upon the results of ultrafiltration.

It is evident from Fig. 2a that all three regions are of different hydrogen-ion concentration, that of the dialyzate being calculable according to the usual Donnan formula for membrane equilibrium based on the average concentration of the other two. The three regions are, therefore, designated in order of decreasing concentration, $C_{\mathrm{H}^+}+$, C_{H^+} and $C_{\mathrm{H}^+}-$. It is obvious that the dialyzate has not the composition of the intermicellar liquid, contrary to the common assumption mentioned in the fourth paragraph of this paper. There is, however, one intermediate rate of ultrafiltration for which the concentration of the ultrafiltrate will be that of the intermicellar liquid, as shown in Fig. 2b. For slower ultrafiltration the results will lie between those of Figs. 2a and 2b.

For more rapid ultrafiltration the results will tend toward that illustrated in Fig. 2c. In other words, when ultrafiltration is pushed as rapidly as possible, it will encroach upon all regions of the solution and more nearly represent the average cross-sectional concentration of the filterable constituents within the sol. This well accounts for the low concentration of ultrafiltrate obtained in quick ultrafiltration and the relatively high concentrations obtained with slow ultrafiltration and dialysis.

Even in the most rapid ultrafiltration, owing to the enormous electrostatic forces otherwise involved, there must remain with the colloidal charges an equal number of oppositely charged free ions which cannot be filtered. This then does not affect the argument. The PH of a very rapidly obtained ultrafiltrate must be less than that of the original "ferric hydroxide" sol. In our work the PH of sol 13[9] corresponded to a hydrochloric acid concentration of $5.0 \times 10^{-5}\ N$, while from Table II it is seen that rapidly obtained ultrafiltrate contains only $2.8 \times 10^{-5}\ N$. At the other extreme the far higher concentration of 18×10^{-5} N was found for the dialyzate.

At first sight it might seem that even if the regions in the immediate neighborhood of colloidal particles were being encroached upon and robbed in rapid ultrafiltration, this might not greatly affect the total concentrations of ions passing through the filter, since the unequal distribution of positive ions in the domain of the positive colloid is offset by a similar unequal distribution of the same ions in the opposite direction in the neighborhood of the compensating negative ions such as the chloride ions in the present case. If the colloidal particles were monovalent, that is, each particle carried but one electrical charge, then indeed the effects of encroachment and the effects upon PH would disappear.

To produce the effects here uncovered two things are, therefore, necessary: first, that the particles are polyvalent; and, second, that the charges are close together.[12]

In the membrane equilibrium the hydrogen electrode gives the same potential for dialyzate and intermicellar liquid, the difference in concentration being offset by the membrane potential

$$E = \frac{RT}{F} \ln \frac{C_{\mathrm{H}^+}+}{C_{\mathrm{H}^+}}$$

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[12] Compare J. W. McBain [THIS JOURNAL, 50, 1636 (1928)] where it is shown that with the ionic micelle of soap solutions the ionic strength is essentially that only of a uni-univalent salt because of the very wide distance apart of the charges upon any one ionic micelle (20 Å.).

Similarly, the uniform electrode potential within a sol balances the difference of concentration near a colloidal particle as compared with that of the intermicellar liquid by that portion of the electrokinetic potential or potential of the ionic atmosphere embraced between the two points in question

$$\zeta = \frac{RT}{F} \ln \frac{C_{\mathrm{H}^+}}{C_{\mathrm{H}^+}-}$$

Of course, $C_{\mathrm{H}^+}-$ likewise varies from point to point within the domain of the colloidal particle.

It will be interesting to inquire whether these considerations account for the so-called Hammarsten effect. Hammarsten[13] in several instances found by electromotive force ionic concentrations that were not fully revealed in lowering of freezing point. We have just seen that the PH in the neighborhood of positive charges is much less than that in the intermicellar liquid, although both give the same electrode potential, and that thus the concentrations as ordinarily obtained from e. m. f. measurements of colloids are partly fictitious. In this connection it should be pointed out that in our sols the domains of the colloidal charges almost or actually overlap. Thus in many colloidal sols there is no point at which there is true intermicellar liquid, and nowhere then will the real concentration equal the apparent PH or C_{H^+}.

In conclusion, it should be mentioned that Maffia,[14] using a pressure of only a few millimeters, found 60 to 80% of the total conductivity in the ultrafiltrate for sols otherwise closely resembling sol 13. Wintgen and Biltz,[15] also working with sols similar to sol 13, used a pressure of one atmosphere, which gave fairly rapid rates with the membranes used. They found lower conductivities than did Maffia, but still about 30 to 60% of the total conductivity was found in the ultrafiltrate.

Variations in the concentration of the ultrafiltrate would be much less for sols with a higher ratio of simple electrolyte to colloidal electrolyte, for a Donnan equilibrium would then produce only a slight inequality in the distribution of the simple electrolyte. This may account for the failure of previous experimenters to observe such a variation, and for the assertions of Duclaux and Titeica[16] and of Kruyt, Roodvoets and van der Willigen[17] that the concentration of the ultrafiltrate is independent of the rate of ultrafiltration.

Additional Note

It has been very kindly pointed out to us that a graph of specific conductance against pressure is as satisfactory as that given against rate of ultrafiltration and that an alternative explanation might be that the

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(13) E. Hammarsten, *Biochem.* Z., 144, 383 (1924); H. Hammersten, *ibid* , 147, 481 (1924).

(14) P. Maffia, *Kolloidchem. Beihefte*, 3, 85 (1911).

(15) R. Wintgen and M. Biltz, *Z. physik. Chem.*, 107, 403 (1923).

(16) J. Duclanx and R. Titeica, *Compt.* rend., 189, 101 (1929)

(17) H. R. Kruyt, A. C. W. Roodvoets and P. C. van der Willigen, "Colloid Symposium Monograph," 1926, Vol. IV. p. 304

particles are carried down to the filter to form a highly hydrated gel-like mat which pressure might dehydrate, the process being continued by the arrival of new particles from the main body of the sol. This explanation is not, however, necessarily different from that which we have given, although we have stressed the electrical aspects which must exist. Every charged particle is surrounded by an ionic atmosphere, predominantly of opposite sign, and likewise by an atmosphere of polarized or loosely bound water. The two atmospheres in part coincide and overlap. When they are encroached upon through pressure or rapidity of filtration, the filtrate will be correspondingly diluted, as we have found. These atmospheres are spontaneously formed and will do work to maintain themselves. In the interionic attraction theory of electrolytes, about one-half of the lowering of equivalent conductivity as compared with that at infinite dilution is ascribed to this very effect. The forces involved are, therefore, enormous, being of the order of magnitude[18] of 10^5 kilograms per coulomb of charge for a linear movement of 0.02 cm. per minute as in the highest rate of ultrafiltration. Such reaction is evidently strong enough to push the charged particles away, and in fact the membrane does not become coated. Such movement (slippage or seepage) caused by relaxation of the ionic atmosphere would, of course, only take place when the particles became crowded in the immediate neighborhood of the ultrafilter. To discriminate further it will be necessary to carry out experiments with membranes differing greatly in degree of permeability, preferably using different kinds of membranes.

Summary

A series of ultrafiltrations was made with a fairly concentrated, very well dialyzed, ferric hydroxide sol. The concentration of the filtrate was found to vary many-fold with the rate of ultrafiltration, the most rapid rates yielding the lowest concentrations of ultrafiltrate, and a form of dialysis the highest concentration.

It is concluded that in slow ultrafiltration the ultrafiltrate approaches the Donnan membrane distribution due to the presence of charged colloids, whereas in very rapid ultrafiltration the regions immediately surrounding the colloidal particles are invaded and sampled. Thus the P_H of a rapidly obtained ultrafiltrate is less than that of the sol of a positive colloid, whereas with very slow ultrafiltration it is much greater.

It is pointed out that neglect of these considerations necessitates a reinterpretation or recalculation of much of the existing data, not only of ultrafiltration but of the P_H and C_{H^+} and ionic concentrations within all colloidal sols.

STANFORD UNIVERSITY, CALIFORNIA

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(18) M. Le Blanc, "A Text-book of Electro-chemistry" (translation by W. R. Whitney and J. W. Brown), The Macmillan Co., New York, 1920, p. 124; seventh German edition (O. Leiner, Leipzig, 1920), p. 117.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

A Copper Membrane Gas-Molecule Sieve. Callendar's Theory of Osmosis

BY D. L. WARRICK AND EDWARD MACK, JR.

For many years large numbers of investigators have been interested in experimentation and speculation not only on the general subject of the passage of liquids[1] through septa but also, ever since the time of Thomas Graham, on the retention of gases by porous solids, and the transpiration of gases and vapors through porous membranes. Without attempting to give an adequate picture of the present state of the literature in this extensive field, we may merely refer to McBain's monograph, "Sorption of Gases and Vapours by Solids," which includes a bibliography of about six thousand experimental and theoretical papers,[2] and to the recent work of McBain[3] and his students on cellulose and other substances, and to the work of Paneth and Peters[4] and Urry[5] on the permeability of glasses to helium and neon. The idea of attempting to find in nature, or to prepare in the laboratory, membranes of the proper porous structure to act as sieves for gas molecules, would appear to be feasible. For example, if the structure proposed by Astbury for d-tartaric acid is correct to the extent that tunnels actually run perpendicular to the 100 face into the crystal,[6] one might expect to find sieve properties in this crystal. Pauling has also suggested the probability of sieve characteristics in the zeolites,[7] and the presence of wandering "vagabond" atoms and molecules in the lattice of the ultramarines, demonstrated by Jaeger[8] and his collaborators, suggests further available porous working substances.

It is well known that zinc[9] can be selectively distilled from brass, and it occurred to the authors that a copper membrane possessing interesting sieve properties might thus be prepared. The present paper gives a

(1) For example, see Zsigmondy, "Colloid Chemistry (Alexander)," Vol. I, Chemical Catalog Co., New York, 1926, p. 944; Manegold and collaborators, *Kolloid-Z.*, 65,273 (1931), etc.; Bartell and collaborators, J. *Phys. Chem.*, **32**, 1553 (1928), and other papers; Michaelis, "Molecular Sieve Membranes," "Fifth Colloid Symposium Monograph," 1927, p. 135; *Natl. Research Council Bulletin*, **69**, 119 (1929); Manning, "The Preparation of Nickel Membranes for Ultrafiltration," J. *Chem. Soc.*, 1127 (1926); and many other papers by many other authors.

(2) J. W. McBain, "Sorption of Gases and Vapours by Solids," G. Routledge and Sons, Ltd.. London, 1932

(3) McBain, *Kolloid.-Z.*, 40, 4 (1926); "Fourth Colloid Symposium Monograph," 1926, p. 11; "Persorption and Monomolecular Sieves," *Trans. Faraday Soc.*, **28**, 408 (1932); McBain and Kistler, *J. Phys. Chem.*, 33, 1806 (1929); 35, 130 (1931). See also Schmidt, Z. *physik. Chem.*, **133**, 263 (1928); Weigel and Steinhoff, Z. *Krist* , **61**, 125 (1924); Tammann, Z. *physik. Chem.*, **27**, 323 (1898).

(4) Paneth and Peters, Z. *physik. Chem.*, **B1**, 253 (1928).

(5) Urry, THIS JOURNAL, **54**, 3887 (1932). See also, for example, in connection with organic membranes, Wertheimer, *Arch. ges. Physiol.* (Pflüger's), **209**, 493 (1925); Bauer, *ibid.*, 301 (1925); Hill. *Science*, **67**, 374 (1927); Alexejev and Matalskii, *J. chim. phys.*, *24*, 737 (1927); and many others.

(6) Astbury, *Proc. Roy. Soc* (London), **A102**, 506 (1923).

(7) Pauling, *Proc. Nat. Acad. Sci* , **16**, 453 (1930).

(8) Jaeger, *Trans. Faraday Soc.*, **25**, 320 (1929); and other papers.

(9) For example, the papers of Graves and Turner, J. *Chem. Soc* , **101**, 585 (1912); Turner, *J. Inst. Metals*, *7*, 105 (1912).

description of the method of preparation of the porous copper membrane and of some of the results secured by testing its porosity to various gases and vapors.

Experimental

Preparation of Porous Copper Membrane.—Pieces (2.5 X 4 cm.) of shim brass about 0.0028 cm. thick were placed in a quartz tube (2.5 cm. diameter) inside a horizontal electric resistance furnace. The quartz tube was sealed, through a cold trap (solid carbon dioxide), to a mercury vapor pump and a McLeod gage. The usual vacuum which was maintained was about 10^{-4} mm. Different pieces of brass were heated at different temperatures ranging from 400 to 900"; and the zinc, which distilled from the brass and condensed in the quartz tube just outside of the furnace, was more or less completely removed from the brass during the course of a few hours or a few days, depending on the temperature. At intervals the furnace was moved slightly in such a way as to expose a new section of the quartz tubing to the cooling effect of the air. In this way the remaining zinc deposited out on an entirely clean surface, and the progress of the distillation could be watched very nicely. At the end of the distillation the copper membrane which was left in the furnace was removed, its loss of weight determined (in some instances a small piece of it analyzed for zinc), and then the membrane was tested for gas molecule porosity in a manner now to be described.

Determination of Membrane Porosity.—A circular piece of the copper membrane, about 15 mm. in diameter, was cut out and mounted[10] in a specially made pipe coupling. The two large-surfaced pipe ends, between which the copper membrane was interposed, were polished steel, and they could be drawn together with a heavy wrench in such a way that the copper membrane was held clamped athwart the pipe channel in an absolutely leak-proof manner. Each end of the coupling was then connected through a glass tubing spiral to a small gas reservoir of known volume, provided with a mercury manometer. Both sides of the apparatus were pumped out and always allowed to stand for an hour to prove that no leaks were present. The desired gas was then introduced into the high pressure reservoir and allowed to transpire through the membrane into the low pressure reservoir. The rate of gas transpiration was measured by reading both of the manometers, the one on the influx side of the membrane and the one on the efflux side. In this way a further convincing check on the absence of any leak in the system was available. The whole apparatus was set up in a constant temperature room. Quite satisfactory reproducibility of transpiration rates was obtained.

Results and Discussion

The following gases and vapors were employed to test the porosity of the membranes: air, hydrogen, oxygen, nitrogen, water, carbon dioxide, methane, ethane, n-pentane, n-hexane, ethyl ether, benzene. A typical transpiration run is given in Table I.

If no leakage, either in or out, occurs, the product of 26.8 cm. (the total high pressure drop) into 215.0 cc. (volume of high pressure side) should be equal to the product of 19.2 cm. (the low pressure increase) into 292.5 cc. (the volume of the low pressure side). This is approximately true, and becomes exactly true, within the limit of the experimental error, when the volumes are corrected for the shift in the position of the mercury meniscus of the two manometers.

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[10] See Schumacher and Ferguson, THIS JOURNAL, 49, 427 (1927).

TABLE I

TRANSPIRATION OF AIR THROUGH COPPER MEMBRANE

Membrane No. 3, first piece

Volume of high pressure side, 215.0 cc.; low pressure side, 292.5 cc. Inside diameter of coupling, 7.94 mm. Temp., 25.5°.

Time, min.	High pressure, p_h, cm.	Low pressure, p_l, cm.	P, cm. $p_h - p_l$	$k = \ln (P_0/P)/t$
0	75.8	0.1	75.7	..
3	75.5	.25	75.35	(1.55 X 10^{-3})
5	75.2	.4	74.8	2.39
8	74.9	.6	74.3	2.33
12	74.5	1.0	73.5	2.45
15	74.2	1.2	73.0	2.42
20	73.75	1.6	72.15	2.40
28	72.85	2.25	70.60	2.33
38	71.85	3.0	68.85	2.49
50	70.7	3.8	66.9	2.46
60	69.8	4.5	65.3	2.46
73	68.6	5.3	63.3	2.45
103	61.3	10.3	51.0	2.42
192	59.4	11.9	47.5	2.43
220	58.1	12.75	45.45	2.43
242	56.15	14.2	41.95	2.44
338	51.3	17.6	33.7	2.41
394	49.00	19.3	29.7	2.48
			Av. =	2.42 X 10^{-3}

It will be noted, in the last column of the table, that the constancy of the transpiration constant is good. This is typical of nearly all of the tests with other membranes and other gases. The fact that the equation $-dP/dt = kP$, where P is the pressure difference on the two sides of the membrane ($p_h - p_l$), holds throughout the whole course of the transpiration means that the flow is *molecular* and not *viscous*. This is indeed to be expected since the mean free paths of the gas molecules, even at atmospheric pressure, are certainly much larger than the effective diameters of the pores in the copper membrane.

Different test pieces cut from the same membrane sample sometimes showed distinctly different porosities, although they always lined up in the same order with respect to porosity to different gases. For example, in Table I, the "first piece" cut from Membrane No. 3 is tested. In Table II, the "second piece" cut from the same membrane will be observed to show a different porosity to hydrogen gas. The difference could hardly be due to variation in thickness in the shim brass, although micrometer measurement showed that this sometimes amounted to several per cent. The thickness of the copper membrane after distillation of the zinc was the same, as nearly as it could be measured, as that of the original brass foil. The differences in porosity within a given membrane sample are probably to be accounted for in terms of slightly different furnace conditions around the sample during preparation. Table II indicates the general effect of the time and temperature of furnacing on the porosity characteristics of the membrane.

TABLE II

EFFECT OF TEMPERATURE AND TIME FACTORS ON POROSITY

Sieve no.	Furnace **temp,** °C.	**Time** of heating, hr.	Loss of wt., %	**Av.** k for H_2	**Av.** *k* for N_2
4	400	24	3.54	Not porous	
3 (first piece)	475	$26^1/_2$	260	5.64×10^{-3}	......
3 (second piece)	475	$26^1/_2$	26.0	2.14×10^{-3}	6.78×10^{-4}
2	500	2	..	Not porous	
9	550	$24^3/_4$	31.43	1.00×10^{-3}	2.54×10^{-4}
8	600	19	37 7	8.17×10^{-3}	$5\ 21 \times 10^{-3}$
12	900	7	46.0	3.08×10^{-2}	8.96×10^{-3}

The brass employed for the preparation of the membranes was found, by chemical analysis, to contain **32.3%** zinc. At the lower temperatures even prolonged distillation failed to remove all of the zinc. At the higher temperatures, in the range 600–900°, not only was the zinc removed, but also some of the copper, which could be seen to condense in the cooler part of the quartz tube, a little nearer to the furnace than the zinc. The membranes prepared at 600–900° were far more porous to the small molecule gases then membranes made at lower temperatures, and they would readily pass large molecules, such as benzene and ethyl ether, which the low-temperature membranes would not allow to pass at all. In Table III are listed the relative porosities to different gases, in terms of the transpiration constant, of a low-temperature membrane.

TABLE III

POROSITY TO DIFFERENT GASES OF LOW-TEMPERATURE MEMBRANE

Membrane No. 3 (475°), Second Piece

Gas	**Average** *k*	Loss in porosity **to** N_2, %
Nitrogen	6.78×10^{-4}	
Hydrogen	21.4	0
Carbon dioxide	6.67	0
Methane	8.80	0
Ethane	7.69	2
n-Pentane	2.86	65
Benzene	0	100
Ethyl ether	0	100

After our porosity testing technique had been standardized it was found desirable to employ nitrogen as a comparison gas, and to redetermine the porosity of the membrane to nitrogen after every exposure to any other gas, in order to discover whether any change might have occurred in the porosity characteristics of the membrane. This procedure worked very satisfactorily; and indeed it was found, as shown in Column **3** of Table **III,** that the larger molecule gases which transpire through the membrane with difficulty, or not at all, reduce the porosity. Very likely this is due to a partial clogging of the pores, or to adsorption at the surface of the membrane, or both. At any rate it was always possible to restore the membrane to its original condition by a vacuum heat treatment (for three hours) at 400°.

It is obvious from Column 2 of Table III that the smaller molecules transpire more readily then the larger ones, and that molecules above a certain size do not transpire at all.

Size of Pores

Microscopic observation (magnification 2700 diameters) fails to show the presence of any visible pore openings on the surface, even of the more highly porous copper membranes prepared at 900°. Since the transpiration, as already shown, is undoubtedly a molecular rather than a viscous flow, and since the equation for molecular flow would probably not hold as well as it is observed to hold unless the mean free path of the transpiring molecule is quite large compared with the average pore diameter, we are probably justified in assuming that the mean free path is at least *ten times* larger than the pore diameter. The mean free path for these gaseous molecules is roughly about 10^{-5} cm., and thus we may fix an upper limit to the pore diameter of approximately 10^{-6} cm., or 100 Å. Very likely the diameter is considerably smaller than this.

The fact that the gaseous benzene molecule, with a greatest distance of about 6 Å. across the ring,[11] fails to transpire through the membrane (Table III) in measurable amount might be taken as indication that the large pores have a diameter not much greater than 6 Å. Of course it is possible that the whole internal network of pores and tubes becomes lined with an adsorbed layer of benzene; and in that case, the actual diameter of the copper pores might be as large as 10–20 Å. without allowing benzene to pass through.

Dr. Herzfeld and Dr. Smallwood have given a detailed discussion of the kinetic theory of transpiration. It is interesting, in the present situation, to apply their Equation 307, which emerges from Knudsen's theory, and which gives the rate of flow in moles of gas:[12]

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{B'}{\sqrt{MRT}}(p_h - p_l)$$

Here, M is the molecular weight of the gas, and B' has the dimensions of an area and depends on the size and shape of the virtual tubes in the porous network of the membrane and not on the gas. Herzfeld and Smallwood cite the work of Graham upon the passage of gases through porous plates of gypsum and meerschaum in support of the above equa-

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(11) Mack, THIS JOURNAL, 54, 2141 (1932).

(12) Herzfeld and Smallwood, Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 2d. ed., 1932, p. 73.

tion. In Table IV the transpiration constants of Table III, obtained with a low-temperature copper membrane, are so treated that the rates of flow of the different gases may be compared with that of hydrogen, taken as unity; and so that the *observed* relative rates may be compared with those calculated from the above equation. It is to be noted that, in the Knudsen theory, the rate of molecular flow does not depend on the molecule cross-sectional area, and is inversely proportional to the square root of the molecular weight.

TABLE IV

OBSERVED AND CALCULATED RELATIVE RATES OF FLOW

Membrane No. 3, Second Piece

Gas	Average k	Molecular wt.	Observed rate (for H_2 set equal to 1)	Calcd. rate (for H_2 set equal to 1)
Nitrogen	6.78×10^{-4}	28	0.32	0.27
Hydrogen	21.4	2	1	1
Carbon dioxide	6.67	44	0.31	0.21
Methane	8.80	16	.41	.35
Ethane	7.69	30	.36	.26
n-Pentane	2.86	72	.14	.17

It is a little disturbing to note, in Table IV, that the observed relative rates (with the exception of pentane) are *larger* than those calculated. If it were the other way around, one might possibly find a plausible explanation in terms of the entrance of the factor of molecule cross-sectional area, in these excessively small pores. It would seem either that the rates of flow of nitrogen, carbon dioxide, methane and ethane are, for some reason, more rapid than they ought to be, or that hydrogen transpires more slowly than it should. In view of the relatively small accommodation coefficient of hydrogen, such a result is difficult to understand. On the whole, however, the agreement between calculated and observed rates is not bad, and is perhaps as good as one could reasonably expect in such a complicated structure of exceedingly small pores. The fairly satisfactory correlation between the last two columns of Table IV argues for a fairly uniform size of the gas channels. For, if there were a considerable dispersion of sizes among the pores which are actually large enough to pass hydrogen and the smaller molecules, we should expect the values for the large molecules of Column 4 to be much smaller relative to those of Column 5 (Table IV), than in the case of the small molecules; but such is not the case (with the exception of pentane).

In a membrane prepared at the *higher temperatures* (600–900°) the zinc atoms undoubtedly tear their way out of the brass lattice more violently than at lower temperatures, and this effect together with the partial volatilization of the copper and the probable realignment of internal structural features due to the play of surface tension and sintering forces would naturally lead to larger channels and to a more porous membrane.

It is interesting to indulge in a little speculation in a rough attempt to estimate the population of pores per unit area. For this purpose let us imagine that the porosity is due to a system of tiny cylindrical capillary tubes running from one face of the membrane to the other. If we take d, the average capillary diameter as 10 Å., and p_h as a pressure of one atmosphere and p_l as zero pressure, we may calculate the rate of flow of hydrogen in moles per second through a single capillary by using Knudsen's equation (Herzfeld and Smallwood, Equation 304)

$$\frac{dn}{dt} = \pi(d/2)^2 \frac{4d}{3L} \frac{1}{\sqrt{2\pi MR}} \frac{p_h - p_l}{\sqrt{T}}$$

where L is the length of the capillary. Because of the probable tortuosity of the capillary channels we might do well to set L equal to about twice the thickness of the membrane, namely, 2 X 0.0028 cm. The calculation gives about **3.3** X 10^{-19} mole per second, or about 2.0 X 10^{-17} mole per minute, which is equivalent to about 1.2 X 10^7 molecules of hydrogen per minute through a single capillary, or about 4.9 × 10^{-13} cc. at 76 cm. and room temperature. Now with Membrane No. **3** (Table III), about 0.54 cc. of hydrogen per sq. cm. of membrane per minute passed through when p_h was 1 atm. and p_l was zero (k = 21.4 X 10^{-4}). It follows therefore that the number of capillaries per sq. cm. of membrane surface would have to be about 10^{12} to explain the observed rate of flow. This would mean about 10^6 capillaries per cm., or capillaries of diameter 10 Å. spaced about 100 Å. apart. This seems reasonable enough. The volume of 10^{12} capillaries of this sort would be about 4.5 X 10^{-5} cc., or about one-sixtieth of the total volume of the membrane (1 X 0.0028 cc.). Since the volume occupied by the zinc atoms in brass of composition **32.3%** zinc would probably be about one-third of the total, this means that roughly one-twentieth of the empty space vacated by the zinc atoms is formed into main artery channels large enough to allow passage to the gas molecules, while the rest of the spaces deserted by the zinc are too small, or too much like blind alleys, to play any part in conducting the gas through the membrane.

While there is, of course, a considerable latitude for choice of the capillary diameter, this simplified but fanciful picture may resemble the actual membrane structure, and leads in effect to the same porosity characteristics actually possessed by the membrane. The same calculation which has here been made for hydrogen flow could be made for any of the other gases. The only difference involved would be the different values of M; and the different calculated absolute rates of flow would be related to one another in the same manner as the relative rates in the last column of Table IV.

Further Experiments

It would be extraordinarily interesting if one could make a porous membrane by means of which it would be possible to separate, by direct sieving, small molecules from large molecules in the gas phase. We have attempted to do this for a mixture of hydrogen and benzene, and for nitrogen and benzene. But, unfortunately, the large benzene molecules, which will not pass through the membrane themselves, also stop the flow of the smaller molecules. When the temperature of the mixture is raised to 400° to drive off the adsorbed benzene molecules, which presumably are plugging the holes, flow begins again, but the membrane almost immediately develops macroscopic lesions and begins to leak. It would not seem impossible, however, to make a membrane which would resist degeneration at 400°, and which would thus be able to perform for mixtures of gas molecules of various assorted sizes the same function that palladium performs for a mixture of hydrogen and nitrogen (although we do not wish to commit ourselves to the view that palladium conducts hydrogen by the same mechanism as the porous copper membrane).

Essentially the same sort of porous membranes have been prepared by distillation of mercury from a dental amalgam, by the removal of water from massive $Al_2O_3 \cdot 3H_2O$,[13] and by the evaporation of various solvents from various cellulose ester[14] films. In the last case the size of the pores seems to be conditioned to a considerable extent by the size of the solvent molecules which escape from the cellulose ester film as it gradually dries out.

The authors have attempted, but so far without success, to carry out a reduction (of nitrobenzene) by generating hydrogen electrolytically at one face of the membrane, and allowing it to transpire through the membrane before coming into contact with the substance to be reduced, in contrast with the usual procedure of generating the hydrogen directly in contact with the reducible substance.

Osmosis

Callendar's Theory.—In his monograph on "Osmotic Pressure" Findlay[15] gives the essence of Callendar's theory of osmosis in the following words: "The semi-permeable membrane consists of fine capillaries which are not wetted by the liquids but which admit of the passage of vapour, or in other words the membrane is a vapour sieve. Since the pure solvent at one end of the capillaries has a higher vapour pressure than in the solution at the other end, distillation will take place from the solvent, and the vapour on passing through the capillary will condense on the surface of the solution. . . ."

We have thought that it would be intensely interesting to test out this theory with our porous copper membrane. For this purpose a membrane (No. 5, second piece) was interposed between water and a 2 M sucrose solution in an osmotic pressure apparatus in a constant temperature room.

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(13) Samples were very kindly supplied to us by Dr. F. C. Frary, of the Aluminum Company of America.

(14) Kindly furnished by Dr. Wm Hale Charch, of the Dupont Cellophane Company.

(15) Findlay, "Osmotic Pressure," Longmans, London, 1913, p. 76.

The osmotic flow was rather slow, and it was found necessary to employ a glass capillary tube in which to observe conveniently the rise of the sugar solution. The *observed rise* over a period of several days was 2.36 cm. in twenty-four hours. The same membrane was then tested for porosity toward water vapor. From the transpiration constant (1.33×10^{-3}) and the known vapor pressures of the water and sugar solution (35.26 and about 32.29 mm. at 31.8°) and the area of the membrane exposed to osmotic flow (58 sq. mm.), the transpiration rate was calculated to be 1.36×10^{-3} g. of water per twenty-four hours. This is equivalent to a *predicted rise* in the capillary of 1.46 cm. in twenty-four hours. In the case of another membrane (No. 5, third piece) a porosity measurement *before* osmosis gave a predicted daily rise of 1.71 cm., that actually observed was 2.72 cm., and a porosity measurement on the same membrane *after* osmosis gave a predicted rise of 1.19 cm.

The observed and predicted rates of osmotic flow agree well enough to make it seem very likely that we have, in the case of porous copper, at least *one* semi-permeable membrane which may actually allow osmosis to occur by the mechanism suggested by Callendar.

The authors desire to express their appreciation to Dr. Saul Dushman of the General Electric Company for helpful suggestions made to us during the writing of this paper.

Summary

The preparation of a porous copper membrane by vacuum distillation of the zinc from thin sheet brass is described.

The porosity characteristics depend on the time and temperature of the preparation. It is shown that the transpiration of a gas through the membrane is a molecular rather than a viscous flow. Typical relative rates of transpiration are given for a number of gases through a membrane which will allow small molecules to pass through but is not porous to benzene and ethyl ether.

The pores, in a typical low-temperature membrane, are probably larger than 6 Å. and smaller than 20 Å. in diameter. A calculation gives the pore population as about 10^{12} per sq. cm.

Callendar's theory of osmosis is tested by interposing a copper membrane between water and a sugar solution. The agreement between the observed and predicted rate of osmotic flow is sufficiently good to make the Callendar mechanism seem plausible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF LIBERAL ARTS,
UNIVERSITY OF CINCINNATI]

Partial Molal Volumes of Cobalt Sulfate and of Cadmium Iodide

BY R. C. CANTELO AND H. E. PHIFER

Masson[1] discovered the empirical linear relation connecting the apparent molal volume, ϕ, of a solute and the square root of the volume molar concentration, c. a and b are constants characteristic of the substance dissolved. Of twenty-four strong electrolytes studied, Masson found that twenty-two of them conformed to equation (1). Geffcken[2] and Scott[3] elaborated upon Masson's work, for uni-univalent electrolytes.

$$\phi = ac^{1/2} + b \qquad (1)$$

Geffcken found that equation (1) held with great accuracy for a given temperature, for a wide temperature and concentration interval. Scott discussed the constant, b, of equation (1) with respect to the additivity in infinitely dilute solution, of the apparent molal volumes of the ions. He suggested that the constant, a, is a measure of the interionic forces existing in the solution.

Redlich and Rosenfeld[4] derived as a necessary consequence of the Debye–Hückel interionic attraction theory, an equation for the partial molal volume of a strong electrolyte:[5]

$$\bar{V}_1 - \bar{V}_1^0 = qw^{3/2}c^{1/2} - \frac{2qgaw^{3/2}}{\frac{3}{D}\frac{\partial D}{\partial P} - \beta}\left(\frac{2}{D}\frac{\partial D}{\partial P} - \beta\right)c \qquad (2)$$

As a limiting law for dilute solutions, equation (2) becomes

$$\bar{V}_1 = qw^{3/2}c^{1/2} + \bar{V}_1^0 \qquad (3)$$

According to Geffcken[2] and Masson,[1] the linear relation (I) held for a given electrolyte up to fairly high concentrations, but the slope of the curves for electrolytes of the same valence type varied from solute to solute in an apparently characteristic manner. Redlich and Rosenfeld[6] upon examining the best experimental data for uni-univalent electrolytes

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(1) Masson, *Phil. Mag.*, **8**, 218 (1928).

(2) Geffcken, *Naturwissenschaften*, **19**, 321 (1931); *Z. physik. Chem.*, **A155**, 1 (1931).

(3) Scott, *J. Phys Chem.*, **35**, 2315 (1931)

(4) Redlich, *Naturwissenschaften*, **19**, 251 (1931); Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

(5) $\bar{V}_1$ = partial molal volume of solute; $\bar{V}_1^0$ = partial molal volume at infinite dilution; $q = 2.303\,RTh\left(\frac{3}{D}\frac{\partial D}{\partial P} - @\right)w\,;\ = \frac{\Sigma\nu_i z_i^2}{2}$; ν_i = number of ions of the i^{th} kind which are formed from a molecule of electrolyte; z_i = valence of ion of the i^{th} kind; $g = 0.328 \times 10^8$; a = ion radius; D = dielectric constant of solution; P = pressure; β = compressibility of the solution; $h = \frac{1}{2.303}\left(\frac{\epsilon^2}{DkT}\right)^{3/2}\left(\frac{2\pi N}{1000}\right)^{1/2}$; $\epsilon = 4.774 \times 10^{-10}$ e. s. u.; k = Boltzmann constant = 1.371×10^{-6} ergs deg.$^{-1}$; N = Avogadro's number = $6\,062 \times 10^{23}$; T = absolute temperature.

(6) Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).

came to the conclusion that at high concentrations the lines were really curved, and that at great dilution the curves all have the same slope, this slope being approximately that required by theory.

The object of the present investigation was to determine whether the partial molal volumes of cobalt sulfate and of cadmium iodide could be represented by equations of the form of (2) or **(3).**

Cantelo and Payne[7] explained the decrease in the transference numbers of cobalt sulfate, in the concentration range 0.1 to *2* molar, on the basis of formation of complex ions. The presence of complex ions in solutions of cadmium iodide has been postulated by McBain, Van Rysselberghe and Squance,[8] by Tesche and Van Rysselberghe,[9] by Gooding and Walton[10] and by other investigators.

Since equations (2) and **(3)** have been derived from a theory of complete dissociation of strong electrolytes, it is to be expected that solutions containing complex ions will deviate considerably in behavior from that required by these equations. Again, if the partial molal volumes can be represented by an equation, $\bar{V}_1 = kc^{1/2} + \bar{V}_1^0$, the numerical value of k should give a measure of the extent of the deviation, and a possible explanation for this deviation on the basis of complex ions. Finally, the numerical value of $\bar{V}_1^0$ will give, to some extent at least, a measure of the net volume change in infinitely dilute solution due to (a) the breaking down of the crystal lattice, (b) the effect of the ionic field upon the dipole water molecules.

Experimental Part

Cobalt Sulfate.—"International Critical Tables" gives values for the densities, 25°/4°, of cobalt sulfate solutions for the range 0.065 to 0.558 molar only. Accordingly, we have used the complete density determinations, 25°/4°, of Payne for the range 0.01 to 2.4 molar.[11]

The partial molal volumes of water, $\bar{V}_2$, in this range of concentration were determined according to the "method of intercepts" described by Lewis and Randall;[12] the corresponding partial molal volumes of cobalt sulfate, $\bar{V}_1$, were calculated from the equation

$$\bar{V}_1 = \frac{\mathbf{V} - \bar{V}_2(1 - x)}{x} \tag{4}$$

$\mathbf{V} = V/(n_1 + n_2)$, where V is the volume of the solution containing n_1 and n_2 moles of solute and solvent, respectively, x is the mole fraction of solute. The results obtained are given in Column **3** of the data for cobalt sulfate given in Table I.

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[7] **Cantelo and Payne,** *J.* **Phys.** *Chem.,* **36, 1045 (1932).**

[8] **McBain, Van Rysselberghe and Squance,** *ibid.,* **35, 999 (1931).**

[9] **Tesche and Van Rysselberghe, Trans.** *Am. Electrochem. Soc.,* **59, 333** (1931).

[10] **Gooding and Walton,** *J.* **Phys.** *Chem., 35,* **3612 (1931).**

[11] **Payne. Dissertation, University of Cincinnati, 1931.**

[12] **Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., 1923, p.** 38

Cadmium Iodide.—Density determinations, 25°/4°, are given in "International Critical Tables" for the concentration range 2 to 45% CdI_2. However, on account of the straight line relationship obtained, when the values of V calculated from these data were plotted against the mole fraction, x, of cadmium iodide, we determined densities for thirteen interpolated concentrations. Finally, twenty-five points were used to determine the functional dependence of V on x. It is definitely linear. The "least squares" equation to the straight line obtained was found to be

$$V = 49.09x + 18.07 \qquad (5)$$

$\bar{V}_1$ is thus constant for the whole range of concentration and is found by substituting x = 1 in equation (5). $\bar{V}_1 = 67.16$ (see Table I).

Potassium Chloride.—For purposes of comparison, particularly with respect to the w factor of equations (2), (3), we have calculated the partial molal volumes of potassium chloride from the equation given for this salt by Gronwall and La Mer[13]

$$\bar{V}_1 = 27.02 + 4.234\, m - 1.4706\, m^2 + 0.20767\, m^3 \qquad (6)$$

m = molality. The results obtained are given in Column 3 of the data for potassium chloride in Table I.

Results Obtained.—Table I contains the complete results for the three salts.

TABLE I

PARTIAL MOLAL VOLUMES AT 25° AND 1 ATM.

Cobalt Sulfate

c	$c^{1/2}$	51 exptl.	$\bar{V}_1$ calcd.
2250	1.500	16.82	17.57
1.954	1.397	16.29	16.13
1.827	1352	15.73	15.49
1.731	1.315	15.12	14.98
1.615	1.271	14 47	14.35
1.511	1.229	1376	13.77
1.389	1.179	13.01	13.06
1.265	1.125	12.18	12.30
1.121	1.059	11.27	11.38
0.9721	0.9858	10.23	10.35
.8752	.9354	8.976	9.64
.7261	.8521	8.264	8.47
,6473	.8044	7.473	7.80
.5301	,7280	6.498	6.72
.3587	.5988	5.271	4.90

Potassium Chloride

c	$c^{1/2}$	$\bar{V}_1$ G & L eqn.	$\bar{V}_1$ calcd.
2.2926	1.5141	31.76	31.63
1.6694	12921	30.95	31.05
0 9187	0.9585	29.73	29.88
.6689	.8179	28.22	29.29
.3342	.5781	28.34	28.29
.2713	.5209	28.13	28.07

Cadmium Iodide

c, 0.005 to 1 molar,
$\bar{V}_1 = 67.16$

The values of $\bar{V}_1$ given in Column 3 of Table I have been plotted against $c^{1/2}$ in Fig. 1. The $\bar{V}_1 - c^{1/2}$ curves are evidently linear for these salts. The best equations for the lines were determined by the method of "least squares." These equations are

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[13] Gronwall and La Mer, J. Phys. Chem., **31, 393 (1927).**

For $CoSO_4$ $\bar{V}_1 = 14.06\, c^{1/2} - 3.514$ (7)
For KC1 $\bar{V}_1 = 3.652\, c^{1/2} + 26.23$ (8)
For CdI_2 $\bar{V}_1 = 67.16$ (9)

Values for the respective $\bar{V}_1$'s calculated from equations (7) and (8) are given in Column 4, Table I. The respective molal volumes for the three solid salts, cobalt sulfate, potassium chloride, cadmium iodide are 44.64 cc., 37.58 cc., 64.88 cc.

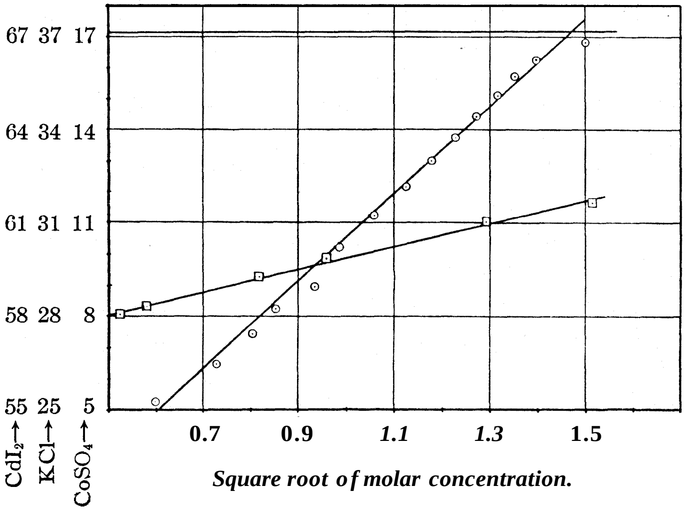

Fig. *1.—Plot of partial molal volumes at* 25°: ⊙, $CoSO_4$; ⊡, KCl.

Discussion of Results

Potassium Chloride.—The factor, *q*, in equations (2) and (3), calculated from Falckenberg's measurements at 16.3° of $\frac{1}{D}\frac{\Delta D}{\Delta P} = 46 \times 10^{-9}$ for the interval 7 to 200 atmospheres, and from $\beta = 49.2 \times 10^{-6}$ and h = 0.497, has the value 2.7 (for 16.3'). Hence the Redlich equation for potassium chloride may be written

$$\bar{V}_1 = 2.7\, c^{1/2} + \bar{V}_1^0 \qquad (10)$$

The agreement of the coefficients of $c^{1/2}$ in equations (8) and (10) can be considered satisfactory, in view of the fact pointed out by Redlich and Rosenfeld[4] that an accuracy of only about 30% can be assigned to the numerical value of q.

If we integrate equation (6) we obtain *V*, the total volume of solution per 1000 grams of water.

$$V = 0.05192\, m^4 - 0.4902\, m^3 + 2.117\, m^2 + 27.02\, m + 1003 \qquad (11)$$

From equation (11) and the other necessary data, we can calculate the contraction per mole of potassium chloride for a solution of molality, m. When this is done we find that this contraction per mole is 7.56 cc. for 2.50 *m* solution and increases to 11.35 cc. for zero concentration.

In a recent paper Pearce and Nelson[14] showed that the fractional vapor pressure lowerings produced by potassium chloride differed least, of all the alkali halides, from the theoretical fractional vapor pressure lowerings calculated on the assumptions that the salts are completely dissociated and that the ions behave as perfect solutes. According to their interpretation this means that in the case of potassium chloride solutions, the ionic field has little effect in causing the dipole water molecules to lose a part of their fugacity.

Since the ionic field in potassium chloride solutions has little effect upon so characteristic a property as the fugacity of the water molecules, it seems plausible to suggest that this field has but little effect also in distorting the dipole water molecules.

In other words, the above decreases in volume produced upon solution of solid potassium chloride can be assigned to the volume change accompanying the physical change, solid to liquid.

We shall, therefore, look upon potassium chloride as an electrolyte whose behavior in solution does not exhibit abnormalities.

Cobalt Sulfate.—The Redlich equation for cobalt sulfate is

$$\bar{V}_1 = 21.6\,c^{1/2} + \bar{V}_1^0 \qquad (12)$$

The discrepancy in the coefficients of $c^{1/2}$ in equations (7) and *(12)* is in the right direction to be explained by the existence of complex ions. According to equation (3), the coefficients of $c^{1/2}$ for potassium chloride and for cobalt sulfate should be in the ratio *1:8*. Actually, they are in the ratio *1:4*. No definite conclusion can be drawn, however, from this investigation, as to whether cobalt sulfate does or does not form complex ions.

When we examine the $\bar{V}_1^0$ value in (7), we find a tremendous discrepancy between it and the value, *44.64* cc., for the solid salt. Masson[1] explains a discrepancy of this kind by assuming hydration of the ions. He says: "The true solute is a hydrate whose molecular volume is $\phi' = \phi + (18.016/d_w)x = b' + ac^{1/2}$." Since actually $\phi = b + ac^{1/2}$ is the relation plotted, $b' = b + (18.016/d_w)x$. Even though $b = \phi^0 = \bar{V}_1^0$ may be negative, the correction added is sufficient to make b' positive. x is "an integer indicated by the composition of the hydrate in question."

For cobalt sulfate, in terms of molality, we have

$$\bar{V}_1 = 13.48\,m^{1/2} - 3.164 \qquad (13)$$

Upon integration we obtain V, the total volume of solution per *1000* grams of water.

$$V = 8.987\,m^{3/2} - 3.164m + 1003 \qquad (14)$$

From this equation, and the other necessary data, we obtain for the contraction per mole of cobalt sulfate, *34.2* cc. for *2.30* m and *48.15* cc. for zero concentration.

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(14) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932).

Evidently in the case of cobalt sulfate we have to consider that the volume changes upon solution are due to the two effects (a) the change from crystal lattice to solution, (b) the effect of the ion field upon the configuration and volume of the water molecules. Measurements of the fractional vapor pressure lowerings produced by cobalt sulfate might give some information as to the relative importance of these two effects.

Cadmium Iodide.—The coefficient of $c^{1/2}$ for cadmium iodide is zero. In other words, cadmium iodide solutions do not conform at all to equations (2) and (3), derived from a theory of complete dissociation. This is one more abnormality to be added to the many exhibited by this salt.[8]

The $\bar{V}_1^0 = \bar{V}_1$ values of cadmium iodide differ little from the molal volume of the solid salt. Evidently, the two effects considered above in the case of cobalt sulfate must be negligible or must neutralize each other in the case of cadmium iodide.

It is interesting to note here the equation given by Longsworth for $\bar{V}_1$ for cadmium chloride[15]

$$\bar{V}_1 = 8.82\, m^{1/2} + 23.24 \qquad (15)$$

The coefficients of $m^{1/2}$ and $c^{1/2}$ will not differ much. $qw^{3/2}$ for cadmium chloride is 14.03; the ratio of the coefficients of equations (8) and (15) is a little over 1:2 Theoretically this ratio should be about 1:5.

Summary

1 The partial molal volumes of cobalt sulfate at 25°, within the range 0.3 to 2.25 molar, have been determined.

2. The partial molal volumes of potassium chloride at 25°, within the range 0.27 to 2.29 molar, have been calculated from the Gronwall–La Mer equation.

3. The partial molal volumes of cadmium iodide at 25°, within the range 0.005 molar to 1 molar, have been determined.

4. Empirical equations have been derived, governing the linear relation between the partial molal volume and the square root of the molar concentration, for potassium chloride, cadmium iodide and cobalt sulfate; and the constants of these equations have been compared with those of the corresponding theoretical equations.

5. A theoretical discussion of the partial molal volume relations of the three salts has been given.

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(15) Longsworth, THIS JOURNAL, 54, 2741 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF STOCKHOLM AND THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

x-Ray Analysis of Iron-Tin Alloys

BY W. F. EHRET[1] AND A. F. WESTGREN[2]

The iron–tin system has been the subject of a number of investigations in the past. The first extensive examination of the system was completed by Isaak and Tammann in 1907.[3] Their thermal analysis led them to the following conclusions: (1) the solubility of tin in iron is 19 weight per cent. at all temperatures up to 1140°, (2) at 1140° and between 50-89% tin, a region of incomplete miscibility exists in the liquid state, *(3)* a compound is formed which undergoes two polymorphic transformations in the solid state. Because of marked segregation in many of their alloys, they were unable to ascribe a definite formula to the compound. In 1926, Wever and Reinecken[4] published the results of a thoroughgoing investigation of the system. They employed the thermal, magnetometric, and microscopic methods of analysis and arrived at an equilibrium diagram which is rather similar to that of Isaak and Tammann. A compound, Fe_3Sn, is supposed to be stable at elevated temperatures and another compound, $FeSn_2$, stable below 890°, is postulated as undergoing three polymorphic transformations as the temperature is varied. It is interesting to note that the diagram of Wever and Reinecken indicates no partial miscibility in the liquid state. According to these experimenters, all that is necessary, to prevent the segregation of alloys of 50–90% Sn into layers of different density, is rapid stirring of the melt followed by quenching. The non-existence of a miscibility gap has, however, been called into question by Ruer and Kuschmann,[5] who examined a 70% Sn alloy and found two distinct layers whose microstructure indicated partial miscibility in the liquid state. More recently, Edwards and Preece,[6] using thermal and microscopic methods, have confirmed the existence of a zone of partial miscibility in the liquid state (see Fig. I). The equilibrium diagram constructed by these investigators differs from that of Wever and Reinecken in the following additional respects: (1) the compound Fe_3Sn is not found, (2) a compound, Fe_2Sn, is stable between 760–900°, **(3)** a compound, FeSn, is stable below 800°, (4) the compound $FeSn_2$ exists only below 496°. The x-ray analysis of this system has yielded results which are in fair agreement with those of the last mentioned workers. The latter have apparently overlooked two phases, the γ and β' of Fig. *3.*

The number of alloys prepared by the authors may be seen from Table I,

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(1) Washington Square College, New York University.

(2) Institute of General and Inorganic Chemistry, University of Stockholm.

(3) Isaak and Tammann, Z. *anorg. Chem.*, **53**, *281 (1907).*

(4) Wever and Reinecken, Z. *anorg. allgem. Chem.*, *161*, 349 (1926).

(5) Ruer and Kuschmann, *ibid.*, 153, *260 (1926).*

(6) Edwards and Preece, J. Iron *Steel Inst. (London).124, 41 (1931).*

which gives a summary of the results obtained in this investigation. Electrolytic iron and Kahlbaum tin were used as starting materials and the melts were made in a vacuum furnace constructed by G. Phragmén of the Metallographic Institute, Stockholm. The furnace is essentially a Tammann furnace operating in vacuum. A glass window in the top of the furnace permitted the simultaneous observation of the temperature (optical pyrometer) and condition of the melt. In each case the temperature was raised to 1550–1570° to ensure complete melting of the iron. Although no mechanical means of stirring was provided, the bubbling and spurting which took place in the melt both before and after the last of the solid had disappeared, was apparently very effective in counteracting segregation such as was noticed by previous workers. Even though the melts were cooled slowly—about an hour was required to come to room temperature—a non-uniform regulus was obtained in only one case, that of the 70% Sn alloy. Several attempts to prepare a uniform alloy of this composition resulted in segregation into two layers of approximately equal bulk. The x-ray analysis showed each layer to consist of practically a single intermetallic phase (the @ and $FeSn_2$ phases).

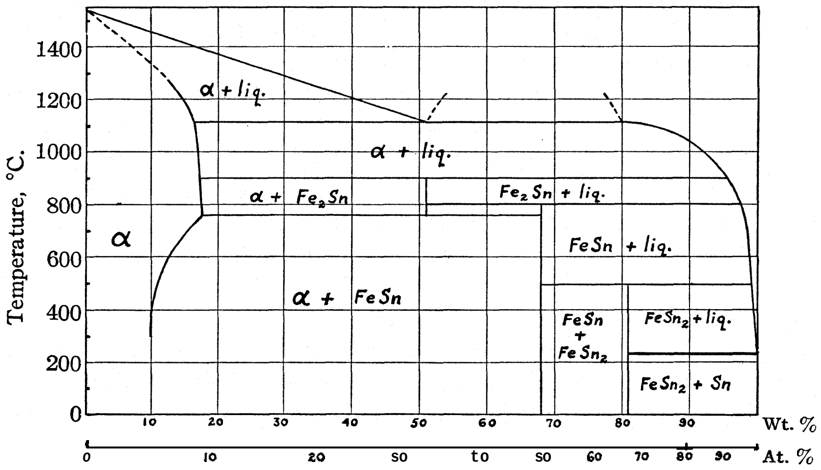

Fig. 1.—Equilibrium diagram of the system Fe–Sn drawn in accordance with the data of Edwards and Preece.

The several alloys were subjected to different heat treatments as is indicated in Table I. The annealing was always carried out upon filings of the original melts sealed in evacuated glass or quartz tubes. That equilibrium was not always established, even after long annealing, follows from the fact that a number of our photograms indicate the presence of three and even four phases. This may be laid in large measure to the tendency toward sintering which is especially pronounced at high temperatures and in alloys of high tin content. Since the powder method of x-ray analysis was to be employed it was necessary to counteract the sintering. The admixture of powdered glass or quartz with the metal filings was found quite effective for this purpose. The glass or quartz was removed subsequent to the annealing by means of a sieve, or the alloy powder was isolated by means of a magnet.

TABLE I

SUMMARY OF X-RAY STUDIES OF IRON–TIN ALLOYS

% Sn	At. % Sn	Heat treatment	Phases	Lattice dimensions
1 0	0.5	Annealed 900°, 1 week Recryst. 650°, 3 min. Air cooled	a	2.864 Å. (pure a-Fe = 2.861 Å.)
3.0	1.5	Ann. 900°, 1 wk. Recryst. 600°, 10 min.	a!	2.871 Å.
7.6	3.7	Ann. 900°, 1 wk. Recryst. 700°	a	2 887 Å.
12.1	6.0	Ann. 900°, I wk. Recryst. 650°, 10 min.	a	2.903 Å
17.6	9.0	Ann. 900°, 1 wk. Recryst. 650°, 10 min.	α	2 921 Å.
27.7[a]	15.5[a]	Ann. 900°, 1 wk. Recryst. 600°, 10 min.[a]	β + a (trace)	β: a_1 = 5.293 Å. a_3 = 4.443 a_3/a_1 = 0.839
27.7	15.5	Ann. 680''. 4 days Quenched	α + β′	α: a_1 = 2.894 Å.
27.7	15.5	Ann. 860°, 2 days Quenched	α + β″ + γ (Sn?)	a: a: = 2.922 Å. β″: a_1=5.449 Å. a_3 = 4.353 a_3/a_1 = 0.80 γ: a_1 = 4.179 Å. a_3 = 5.201 a_3/a_1 = 1.245
27.7	15.5	Ann. 950°, 10 min. Quenched	α + β″ + Sn	α: a_1 = 2.92 Å. β″: a_1= 5.449 Å. a_3 = 4.353 a_3/a_1 = 0.779
39.3	23.5	Ann. 450°, 75 min. Quenched	α + β	a: a_1 = 2.91 Å.[b] β: a_1 = 5.293 Å. a_3 = 4.442 a_3/a_1 = 0.839
39.3	23.5	Ann. 680°, 4 days Quenched	α + 8'	a!: a_1 = 2,896 Å.
39.3	23.5	Ann. 850°, 15 min. Quenched	α + β″ + γ	
39.3	23.5	Ann. 860°, 2 days Quenched	α + β″ + γ + Sn	α: a_1 = 2.925 Å. γ: a_1 = 4.179 Å. a_3 = 5.201 a_3/a_1 = 1.245
39.3	23.5	Ann. 910°, quenched	a + Sn	α: a_1 = 2.924 Å.

TABLE I (Concluded)

% Sn	At. % Sn	Heat treatment	Phases	Lattice dimensions
39.3	23.5	Ann. 920–930°, 5 min. Quenched	a + γ	
48.2	30.4	Ann. 450°, 1 wk. Quenched	β + very little a	
48.2	30.4	Ann. 680°, 2.5 days Quenched	a + β'	a: $a_1 = 2.898$ Å.
48.2	30.4	Ann. 860°, 1 day Quenched	β'' + little Sn	β'': $a_1 = 5.449$ Å. $a_3 = 4.353$ $a_3/a_1 = 0.799$
48.2	30.4	Ann. 950°, 1.5 hrs. Quenched	α + Sn + β''	a: $a_1 = 2.924$ Å. β'': same as at 860°
59.4	40.7	Ann. 450°, 5 days Quenched	β + α (trace)	β: $a_1 = 5.292$ Å. $a_3 = 4.440$ $a_3/a_1 = 0.839$
59.4	40.7	Ann. 660–680°, 2 days Quenched	β'	
81.7	67.7	Ann. 330°, 40 hrs. Air cooled	$FeSn_2$	$FeSn_2$: $a_1 = 5.317$ Å. $a_3 = 9.236$ $a_3/a_1 = 1.737$
81.7	67.7	Ann. 450°, 1 wk. Quenched	$FeSn_2$	
81.7	67.7	Ann. 600°, 2 days Quenched	β + Sn	
81.7	67.7	Ann. 680°, 4 days Quenched	β + Sn	β: $a_1 = 5.291$ Å. $a_3 = 4.437$ $a_3/a_1 = 0.839$
81.7	67.7	Ann. 760–780°	Sn + γ	
81.7	67.7	Ann. 850–870°, 30 min. Quenched	Sn + γ	γ: $a_1 = 4.231$ Å. $a_3 = 5.211$ $a_3/a_1 = 1.232$
90.1	80.0	Ann. 400°, 15 hrs.	Sn + $FeSn_2$	[d]
97.7	95.0	Ann. 400°, 15 hrs.	Sn + $FeSn_2$	[d]

[a] It is probable that the ten minutes at 600° were sufficient to bring about not only a recrystallization but also to establish a new equilibrium characteristic of the lower temperature. A sample of this alloy was annealed at 600° thirty minutes and quenched, whereupon photograms were obtained which indicated the presence of the β and α phases. The positions of the diffraction lines were practically identical with those for the alloy sample which had been annealed at 900° and recrystallized at 600°

[b] Probably no real equilibrium

[c] An alloy containing 71.8% Sn separated into two layers upon cooling. It was probably not in a state of equilibrium. The upper layer, containing 78.9% Sn, produced the diffraction pattern of $FeSn_2$. The lower layer (54.9% Sn) gave the pattern of the β phase.

[d] The constants calculated for Sn were identical with those reported for pure Sn by Westgren and Phragmén [*Z. anorg. allgem. Chem.*, 175, 80 (1928)]. Iron is therefore practically insoluble in tin.

x-Radiation was obtained from an iron anode in a Siegbahn–Hadding type of tube. The cameras were of the focusing type and constructed according to the specifications of G. Phragmén. The mean error of the parameter values given is estimated at 0.002 Å.

The Alpha Phase

From Table I and Fig. 2 it is apparent that a-iron dissolves increasing amounts of tin as the temperature is raised. The value of a_1, the length of the cube edge in the body-centered *a-Fe* lattice, increases linearly with the concentration of tin. At 680° the solubility of tin in iron is 9.8%, corresponding to $a_1 = 2.896$ Å. At about 900" the solubility has increased to 18.8%, corresponding to $a_1 = 2.925$ Å.[7] At higher temperatures the solid solubility is very likely even greater.

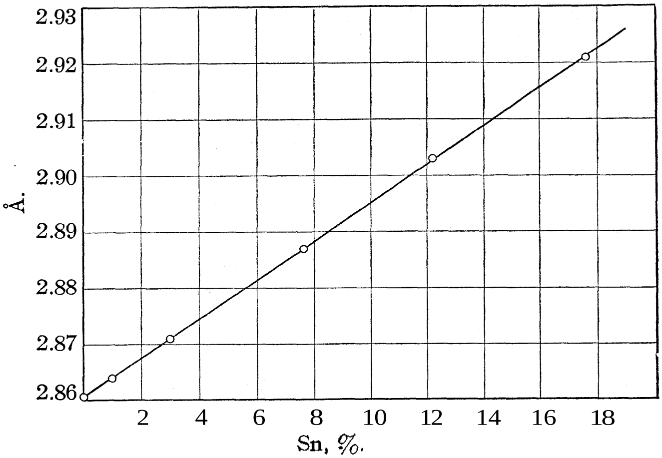

Fig. 2.—Expansion of α-Fe lattice as tin is dissolved.

The Beta Phase

Figure 3 represents roughly the results obtained in this investigation. The broken lines are simply indications of probable phase boundaries. As the Sn concentration is increased at low temperatures, the α phase is followed by a two-phase range in which α appears along with a phase we have called β (corresponds to FeSn of Edwards and Preece). The crystal lattice of the latter possesses hexagonal symmetry. The dimensions of the unit cell show practically no change with temperature or composition and this may be taken to mean that the β phase has a very narrow homogeneity range. Confirmation of this point is obtained from an examination of the diffraction pattern of the lower layer of the 71.8% Sn alloy, annealed at 480°. The pattern shows that the diffraction lines of the β phase correspond, within the limits of error, with those found on photograms of alloys

(7) Compare A. F. Westgren, *Trans. Am. Inst. Min. Met. Eng., Inst. Metals Division,* 14 (1931).

in which β is in equilibrium with α. The cell constants of the β phase as calculated from the photograms of the 59.4% Sn alloy, are: a_1 = 5.292 Å., a_3 = 4.440 Å., a_3/a_1 = 0.839. The volume of the unit cell is therefore 107.6 A.3 Since the aforementioned alloy still contains traces of the a-phase, it is probable that the composition of the 8-phase corresponds to FeSn (68% Sn). The density of the 59.4% Sn alloy, after

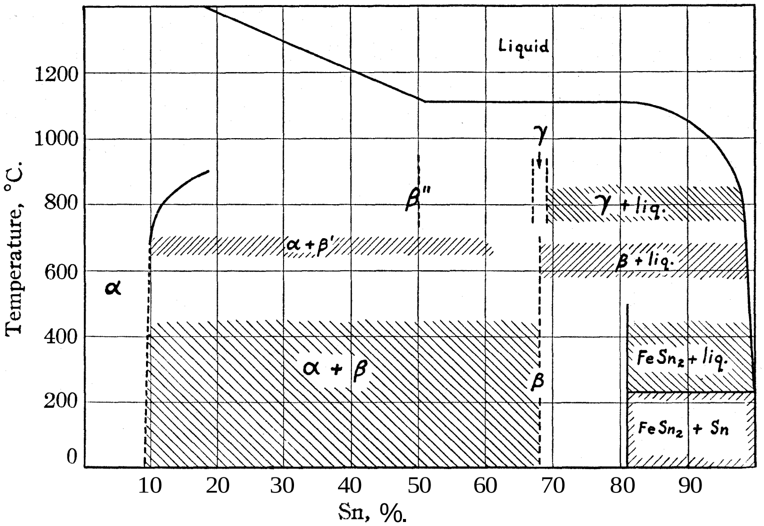

Fig 3.—Schematic phase diagram of the system Fe–Sn.

tempering for a week at 370°, was 7.54 g. per cc. If the alloy is considered homogeneous, calculation gives 6.04 atoms per unit cell. In view of this it seems most probable that there are six atoms (three groups of FeSn) in the elementary prism of the β phase. Table II is typical of the results obtained in this investigation. In it the observed $\sin^2 \Theta/2$ values for the

TABLE II

DATA TAKEN PROM PHOTOGRAMS OF THE 59.4% SN ALLOY (β PHASE) ANNEALED AT 450" FOR FIVE DAYS AND QUENCHED

Intensity	FeK radiation	$h_1h_2h_3$	$\sin^2 \Theta/2$ observed	$\sin^2 \Theta/2$ calculated
s.	a!	101	0.0917	0.0918
w.	β	110	.1092	.1098
s.	a	110	.1332	.1335
v. w.	β	111	.1486	.1488
w.	β	002	.1559	.1562
w.	a	200	.1780	.1780
w.	α	111	.1808	.1808
w.	β	201	.1855	.1855
m.	α	002	.1892	.1892
v. w.	α	110 (αFe)	.2200	.2200
v. s.	a	201	.2251	.2253

TABLE II (Concluded)

Intensity	FeK Radiation	$h_1h_2h_3$	Sin^2 $\theta/2$ observed	Sin^2 $\theta/2$ calculated
m.	β	112	0.2685	0.2660
w.	β	121	.2972	.2953
v. w.	β	202	.3040	.3026
v. w.	α	210	.3128	.3115
v. s.	α	112	.3248	.3227
v. w.	β	300	.3309	.3294
s.	α	121	.3607	.3588
m.	α	202	.3693	.3672
w.	β	103	.3901	.3881
m.	α	300	.4027	.4005
w.	β	220	.4411	.4391
m.	α	301	.4494	.4478
v. w.	β	113	.4623	.4613
m.	α	103	.4723	.4702
w.	β	302	.4871	.4856
w.	β	203	.4986	.4979
w.	β	311	.5165	.5148
s.	α	220	.5354	.5340
m.	α	113	.5615	.5592
m.	α	302	.5908	.5897
w.	β	222	.5965	.5953
v. s.	α	203	.6062	.6037
s.	α	311	.6274	.6258
m.	α_1	311	.6253	.6258
m.	α_2	311	.6281	.6275
s.	α_1	222	.7235	.7232
s.	α_2	222	.7266	.7258
m.	α_1	213	.7376	.7372
w.	α_2	213	.7407	.7411
s.	α_1	401 004	.7592	.7568 .7573
m.	α_2	401 004	.7628	.7613 .7624
v. w.	β	204 or 410?	.7693	.7712 .7685
w.	α_1	303	.8269	.8262
v. w.	α_2	303	.8303	.8303
s. (diff.)	α_1	114 321	.8912	.8903 .8928
m. (diff.)	α_2	114 321	.8952	.8962 .8951
v. w.	α_1	402	.9014	.9012
v. w.	α_2	402	.9053	.9042
w.	β	412	.9259	.9247
m.	α_1	204 or 410?	.9348	.9348 .9345

s. = strong. v. s. = very strong. m. = medium w. = weak. diff. = diffuse.

β phase are compared with those calculated from the following quadratic form characteristic of the hexagonal system.

$$(K_{\alpha_1}) \qquad \sin^2\frac{\theta}{2} = 0.0445(h_1^2 + h_1h_2 + h_2^2) + 0.0473h_3^2$$

For K_{α} the corresponding constants in the equation are: 0.0446, 0.04765, and for K_{β}: 0.0366 and 0.03905. In Fig. 4 may be seen the photograms of the most deviated diffraction lines of this as well as the other phases encountered in the system.

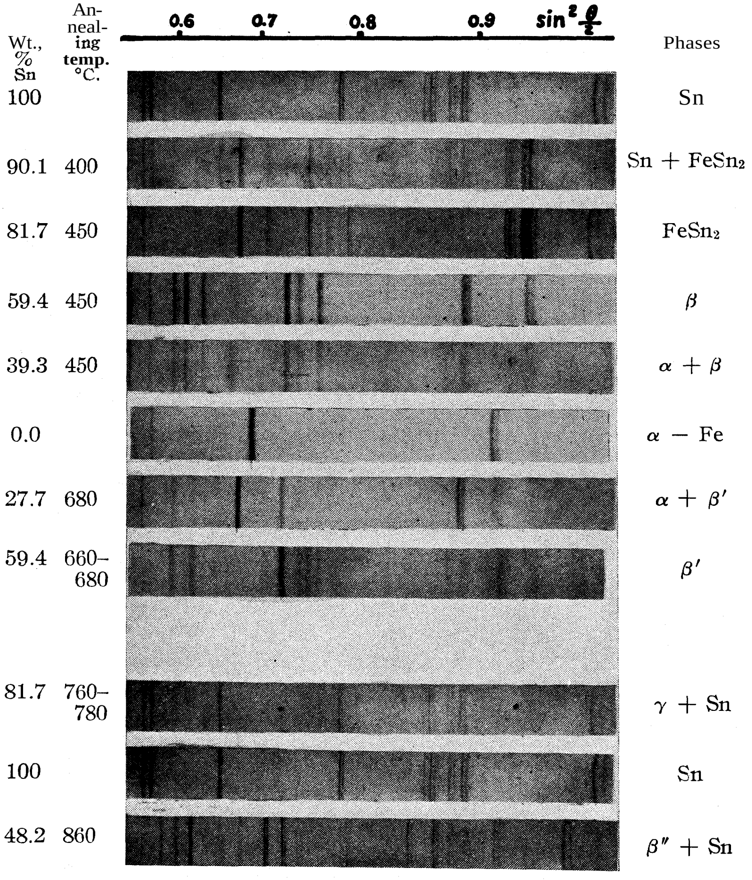

Fig. 4.—Powder photograms of Fe–Sn alloys annealed at various temperatures.

The $FeSn_2$ Phase

The alloy containing 81.7% Sn yielded the diffraction pattern of a single phase after annealing at 330 or 450°. The same pattern was found, together with Sn, for alloys containing 90.1 and 97.7% Sn, when annealed at

400°. The upper layer of the 71.8% alloy, when annealed at 450°, also produced diffraction lines identical with those of the 81.7% alloy. All of these facts indicate that a phase possessing a very narrow homogeneity interval is stable at a composition corresponding almost exactly to $FeSn_2$ (81.0% Sn). This phase, like the β phase, belongs to the hexagonal system. The dimensions of the unit prism are: $a_1 = 5.317$ A., $a_3 = 9.236$ A., $a_3/a_1 = 1.737$, and the volume is 226.1 Å^3. The density of the unannealed alloy was 7.60 g./cc. which gives, by calculation, 10.7 atoms per unit cell. It is likely that this is low, since the alloy in this condition contained considerable tin (density 7.31 g./cc.). Annealing produced a very brittle and porous structure whose density was difficult to determine. The authors are of the opinion that the unit cell of the $FeSn_2$ phase contains twelve atoms (4 $FeSn_2$).

The quadratic equation reproducing the observed $\sin^2 \Theta/2$ values and leading to the constants given for the unit cell size, is:

$$(K_{\alpha_1}) \qquad \sin^2 \frac{\Theta}{2} = 0.04402(h_1^2 + h_1h_2 + h_2^2) + 0.01094h_3^2$$

The corresponding constants for K_{α_2} are: 0.04419, 0.01101, and for K_β, 0.03628, 0.00900.

The Beta' Phase (or Phases)

Alloys containing 27, 39, 45 or 59% Sn, when annealed at 680°, all gave rise to a diffraction pattern which characterizes the β' phase. From the powder data alone, the authors have not been able to discover the symmetry and dimensions of the unit cell of this phase. The well-known graphical methods of Hull and Davey and the more recent graphical method of Bjurstrom have not given any clue[8] to the structure of the β' phase. In view of the difficulty experienced in obtaining a quadratic form satisfying the $\sin^2 6/2$ values of the β' phase, the authors consider it possible that the diffraction pattern is in reality due to a mixture of two phases. Opposed to this view, however, stands the fact that the relative intensities of the lines of the β' pattern remain practically the same whether the alloy contains 27, 39 or 48% Sn.

The Beta" Phase

The powder photograms of alloys containing 27, 39 or 48% Sn and annealed at 860°, all contain the β'' phase (corresponds to Fe_2Sn of Edwards and Preece) among other phases. The phase is also present in the 27 and 48% alloys when quenched from 950°. A glance at the summary of results will show that the alloys quenched from this region of the temperature-composition diagram were usually not in equilibrium, *i. e.*, three and even four phases were present. Two explanations may be given for this: (1) liquation, or the formation of tin-rich liquid during the annealing, and

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(8) Bjurström, Z. *Physik*, **69**, 346 (1931).

(2) the possibility that transformations took place in the time that elapsed between withdrawal from the annealing furnace and entrance into the quenching bath. The absence of equilibrium has made it difficult to single out the region of the equilibrium diagram in which the β'' phase will be stable. Tentatively it may be said that the phase can exist between 750 and 950°.

On all the photograms containing it, the β'' phase presents the same diffraction pattern, and there is therefore no variation in the dimensions of the unit cell. There exists, presumably, a very narrow homogeneity range for the phase. The latter crystallizes in the hexagonal system and the size of the unit cell may be calculated with the aid of the constants given in the quadratic forms below. The dimensions are: $a_1 = 5.449$ Å., $a_3 = 4.353$ Å., $a_3/a_1 = 0.799$. The volume of the unit cell is 111.9 Å^3. The alloy containing 48% tin (860°) comes nearest to containing only β''. The density of this alloy, 7.68 g./cc., gives by calculation 6.7 atoms per unit cell. It is likely that the number of atoms is six and that the slightly larger number found is to be attributed to having used a value for the density that was too high. The density measurements were made upon a piece of the alloy that was in low-temperature equilibrium, *i.* e., contained the β and the relatively heavy α phase. The composition of the 48% alloy corresponds closely to Fe_2Sn (51%) and it is probable that the unit cell of β'' contains two groups of Fe_2Sn. The β'' phase differs only very little from the β phase in dimensions and volume of the unit of structure. Quadratic forms which will give the $\sin^2 \Theta/2$ values are

$$(K_{\alpha_1}) \qquad \sin^2 \frac{\Theta}{2} = 0.0419(h_1^2 + h_1h_2 + h_2^2) + 0.04925h_3^2$$

$$(K_{\alpha_2}) \qquad \sin^2 \frac{\Theta}{2} = 0.0421(h_1^2 + h_1h_2 + h_2^2) + 0.04945h_3^2$$

$$(K_{\beta}) \qquad \sin^2 \frac{\Theta}{2} = 0.0345(h_1^2 + h_1h_2 + h_2^2) + 0.04055h_3^2$$

The Gamma Phase

According to V. M. Goldschmidt the nickel arsenide type of crystal structure is to be looked for whenever we have the possibility of union between a transition element and an element whose atoms are large and easily polarized. Iron and tin furnish such a pair. In a large number of related systems, such as Fe–Sb, Fe–Se, Fe–S, Cu–Sn, Au–Sn, Ni–Sn, etc., a phase having the characteristic nickel arsenide structure exists. In the Fe–Sn system such a phase (γ) has been found in alloys containing 27, 39 and 81% Sn, when quenched from 750–900°. Although no homogeneous alloy was obtained, it is assumed that the composition range of the phase lies close to FeSn (68% Sn). It is possible, however, that the homogeneity range does not include this concentration. This was found to be the case

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(9) Goldschmidt, *Ber.*, **60**, 1286 (1927); Trans. *Faraday Soc.*, **25**, 253 (1929).

in the related systems Fe–Sb,[10] Cu–Sn[11] and Ni–Bi,[12] in each of which the nickel arsenide type of phase contains an excess of the atoms of the transition element. The y phase is apparently homogeneous over a small range of concentrations since its unit cell dimensions vary from $a_1 = 4.179$ Å., $a_3 = 5.201$ Å., $a_3/a_1 = 1.245$ on the iron-rich side of the homogeneity interval to $a_1 = 4.231$ Å., $a_3 = 5.211$ Å., $a_3/a_1 = 1.232$ on the tin-rich side. The volume of the unit cell varies from 78.63 to 80.75 Å^3. Since the y phase was not obtained homogeneous, any calculation of the number of atoms per unit celi will necessarily give only approximate results. Using a density value obtained by extrapolation from the densities of the 59.4 and 81.7% Sn alloys, we arrive at 4.15 atoms per unit cell. This is quite close to 4, which is the value to be expected in the nickel arsenide structure. There are, then, two iron and two tin atoms in each elementary parallelopiped. The following quadratic forms serve to calculate the values of $\sin^2 \Theta/2$.

$$(K_{\alpha_1}) \qquad \sin^2 \frac{\Theta}{2} = 0.06964(h_1^2 + h_1h_2 + h_2^2) + 0.0345h_3^2$$

$$(K,) \qquad \sin^2 \frac{\Theta}{2} = 0.06985(h_1^2 + h_1h_2 + h_2^2) + 0.03465h_3^2$$

The Tin Phase

On all the photograms in which this phase appeared, the diffraction lines occupied positions identical with those of pure tin. Iron and the intermetallic phases already mentioned are, therefore, practically insoluble in tin.

Correlation of the Results with Previous Work

A number of references have already been made to the interrelation of our results and those obtained by other workers. The latest thermal diagram for this system, that by Edwards and Preece, agrees on the whole with the x-ray analysis, but some phases (β' and γ) present at higher temperatures have been overlooked by these investigators. The complete accord existing at lower temperatures leads us to the conclusion that the diagram of Edwards and Preece may be taken as substantially correct below 496". The fact that an alloy containing 82% Sn, when tempered at 600° for two days and then quenched, consists almost entirely of the β and Sn phases, substantiates the conclusion of Edwards and Preece, *i. e.*, that $FeSn_2$ decomposes into FeSn and Sn when heated to *ca.* 496°. Our analysis shows that the solubility of tin in iron falls off more rapidly with temperature than is indicated on the aforementioned diagram or that of Wever and Reinecken. The solubility (Fig. 3) is about 10% at 680° instead of 15% as shown by the previous authors. Figure 3 indicates that the phases

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(10) Hagg, *Z. Krist.*, 68, 470 (1928).

(11) Westgren and Phragmén, *Z. anorg. allgem. Chem* , *175*, 80 (1928).

(12) Hagg and Funke, *Z. physik. Chem.*, *B6*, 272 (1930).

β and β' are formed through transformations in the solid state whereas the $FeSn_2$ is probably formed by reaction of the β phase with the melt. For reasons already stated, the homogeneity ranges of the phases stable at elevated temperatures have not been fixed. It is clear, however, that there are at least four intermetallic phases (a, β', β'', γ) stable in the temperature interval 650–950°. Because of the possibility that β' represents more than one phase, there may be five phases in this interval. The authors are of the opinion that the question of the constitution of Fe–Sn alloys, in the range 10–100% Sn and at temperatures above 496°, is far from settled and that much additional work will be necessary before this portion of the diagram is completed.

Summary

A number of alloys in the system Fe–Sn have been examined by means of the powder method of crystal analysis. The following phases were found.

Alpha Phase.—A solid solution of tin in alpha iron. The solubility at 680° is 9.8% Sn. At 900° it is 18.8%. The length of the cube edge in the body-centered a-Fe lattice increases linearly with the concentration of tin.

Beta Phase.—This phase has a hexagonal structure and a very narrow homogeneity range. The cell constants are: $a_1 = 5.292$ Å., $a_3 = 4.440$ Å., $a_3/a_1 = 0.839$. It is probable that the composition corresponds to FeSn and that the unit cell contains six atoms (three groups of FeSn).

Beta Phase.—Alloys containing 27, 39, 48 and 59% Sn all show the presence of the β' phase after annealing at 680°. With the usual methods, the authors have not been able to discover the symmetry and dimensions of the unit cell of this phase. It is considered possible that the so-called β' phase is in reality a mixture of two or more phases.

Beta" Phase.—Alloys containing 27, 39 or 48% Sn and annealed at 860°, contain the β'' phase. The exact stability range of this as well as the other high temperature phases in the system could not be determined because of the difficulty of obtaining equilibrium in the alloys. The diffraction patterns indicate a very narrow homogeneity interval. The phase is hexagonal and has the following unit cell dimensions: $a_1 = 5.449$ Å., $a_3 = 4.353$ Å., $a_3/a_1 = 0.799$. Density measurements indicate the presence of six atoms in the cell, which makes it probable that there are two groups of Fe_2Sn.

Gamma Phase.—This phase was found in alloys quenched from 750–900" and containing 27, 39 and 81% Sn. It has the nickel arsenide structure and it is assumed that the composition is close to that indicated by the formula FeSn. The dimensions of the unit cell vary from $a_1 = 4.231$ Å., $a_3 = 5.211$ Å., $a_3/a_1 = 1.232$ to $a_1 = 4.179$ Å., $a_3 = 5.201$ Å., $a_3/a_1 = 1.245$ and the phase is probably homogeneous over a small range of concentrations.

$FeSn_2$ Phase.—The photograms of this phase indicate a very narrow homogeneity interval, corresponding almost exactly with the composition $FeSn_2$. The unit cell is probably hexagonal, having the following dimensions: $a_1 = 5.317$ Å., $a_3 = \mathbf{9.236}$ Å., $a_3/a_1 = 1.787$. It is likely that the cell contains twelve atoms, *i. e.*, 4 $FeSn_2$.

Sn Phase.—The diffraction pattern of this phase, as found in a number of our alloys, does not differ from that of pure tin. It follows from this that iron and the other phases in the system are insoluble in tin.

The discrepancies existing between the results of the x-ray analysis and the thermal diagram for the system as set up by Edwards and Preece, have been indicated and discussed.

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Thermodynamic Functions of Hydrocarbon Gases from Spectroscopic Data[1]

BY LOUIS S. KASSEL[2]

Methods

Within the last few years spectroscopic data for numerous diatomic molecules have been used to give very accurate values for those thermodynamic functions which do not involve the absolute value of H. The same methods may be applied to polyatomic molecules; here the spectroscopic data are usually both less accurate and less complete; nevertheless, there seem to be a number of cases in which such calculations may be usefully made. In the present article, methane, ethylene and acetylene will be considered.

The method used has been given in principle by Giauque,[3] but since there are a number of short cuts which may be used when making approximate calculations, the procedure to be followed will be described briefly.

For molecules with energy levels $0, \epsilon_1, \epsilon_2 \ldots$ and associated quantum weights $p_0, p_1, p_2 \ldots$ the Maxwell–Boltzmann distribution law may be written in the form

$$H = -N(\mathrm{d} \log Q/\mathrm{d}\Theta) \qquad (1)$$

where

$$Q = \sum_i p_i \, e^{-\epsilon_i \sigma} \qquad (2)$$

and

$$\Theta = 1/kT \qquad (3)$$

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(2) Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

(3) Giauque, THIS JOURNAL, **52**, 4808 (1930).

Here N is Avogadro's number, and H is the contribution of internal energy to the heat content; likewise, the contributions to other thermodynamic functions are

$$C_p = \partial H/\partial T = R\Theta^2\, d^2 \log Q/d\Theta^2 \tag{4}$$

$$\begin{aligned} S &= \int_0^T C_p\, d \log T \\ &= R \log Q - R\Theta\, d \log Q/d\Theta - R \log p_0 \end{aligned} \tag{5}$$

$$\begin{aligned} F/T &= H/T - S \\ &= -R \log Q + R \log p_0 \end{aligned} \tag{6}$$

It is easily verified that whenever the energy splits up into a sum of independent terms, each of them contributes multiplicatively to Q, and additively to the thermodynamic functions. When the separate energy terms are sufficiently simple in form, the summation in (2) can be handled analytically. The terms into which the energy actually splits are the levels for a rotator or top, plus those for a number of oscillators; in the present treatment, the rotator will be considered rigid, and the oscillators harmonic.

For an harmonic oscillator

$$\begin{aligned} Q &= 1 + e-v + e^{-2\varphi} + \ldots \\ &= 1/(1 - e-P) \end{aligned} \tag{7}$$

where

$$\varphi = h\nu/kT \tag{8}$$

Then

$$H = RT\varphi/(e^{\varphi} - 1) \tag{9}$$

$$S = -R \log (1 - e-v) + R\varphi/(e^{\varphi} - 1) \tag{10}$$

$$F/T = R \log (1 - e-v) \tag{11}$$

It proves convenient in making calculations for polyatomic molecules to use a table of F/T as a function of φ, such as that given by Nernst.[4]

For a rigid rotator

$$Q = \sum_{j=0}^{\infty} (2j + 1)e^{-j(j+1)\sigma} \tag{12}$$

where

$$\sigma = h^2/8\pi^2 JkT \tag{13}$$

For room temperature or higher, σ is quite small, and the greater part of the sum comes from a group of terms with large values of m, the change from term to term in this region being slight. It is then possible to approximate the sum by an integral; the most direct way to do this is to replace $(2j + 1)\, e^{-j(j+1)\sigma}$ by

$$\int_{j - 1/2}^{j + 1/2} (2x + 1)e^{-x(x+1)\sigma}\, dx; \text{ this gives}$$

$$\begin{aligned} Q &= \int_{-\frac{1}{2}}^{\infty} (2x + 1)e^{-x(x+1)\sigma}\, dx \\ &= (1/\sigma)e^{\sigma/4} \\ &= 1/\sigma + 1/4 + \ldots \end{aligned} \tag{14}$$

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(4) Nernst, "Grundlagen d. neuen Warmesätzes," 1918.

There are, however, other ways of replacing a sum by an integral (the inverse of the trapezoidal rule, the parabolic rule, etc.), and when these are used results are obtained which agree only in the leading term. The summation (i2) has been treated by Mulholland[3] by more powerful methods; his result, in the present notation, is

$$Q = 1/\sigma + 1/3 + \ldots \tag{15}$$

Giauque and Overstreet[6] have considered the effect of molecular stretching, and given a convenient approximate method of handling the necessary summations; they show that neglect of this correction would produce an error of about 0.03 cal./mole/degree for hydrogen chloride at 2000°. An error of this magnitude is of course not permissible in their precise calculations, but it is of little importance for the present purposes.

Using Mulholland's result, we obtain for a rigid rotator

$$H = RT(1 - \sigma/3 + \ldots) \tag{16}$$
$$S = -R\log\sigma + R - R\sigma^2/90 + \ldots \tag{17}$$
$$F/T = R\log\sigma - R\sigma/3 + \ldots \tag{18}$$

For a rigid top with three equal moments of inertia we have

$$Q = \sum_{j=0}^{\infty}(2j+1)^2 e^{-j(j+1)\sigma} \tag{19}$$

The first approximation may be obtained by replacing the sum with an integral, as before. In lieu of a correct treatment of this case, such as that given by Mulholland for the rotator, it proves possible to determine the second term in the expansion by numerical examples. The result is

$$Q = \sqrt{\pi}\,\sigma^{-3/2}(1 + \sigma/4 + \ldots) \tag{20}$$

This leads to

$$H = (3/2)RT(1 - \sigma/6 + \ldots) \tag{21}$$
$$S = (R/2)\log\pi - (3R/2)\log\sigma + 3R/2 + \ldots \tag{22}$$
$$F/T = -(R/2)\log\pi + (3R/2)\log\sigma - R\sigma/4 + \ldots \tag{23}$$

For a symmetrical top, with moments of inertia A, A and C, we encounter increasing difficulty. The rotational levels have been given by Reiche and Rademacher[7] as

$$\epsilon_{j,\kappa} = j(j+1)\,\sigma + \kappa^2\tau \quad |\kappa| \leqq j \tag{24}$$

where

$$\sigma = h^2\theta/8\pi^2 A \tag{25}$$
$$\tau = (h^2\theta/8\pi^2)\left(\frac{1}{C} - \frac{1}{A}\right) \tag{26}$$
$$\rho = \sigma + \tau \tag{27}$$

The multiplicity of each $\epsilon_{j,\kappa}$ is $2j + 1$. For this case

$$Q = \sum_{\kappa=-\infty}^{\infty} e^{\kappa^2\tau} \sum_{m=|\kappa|}^{\infty}(2m+1)e^{-m(m+1)\sigma}$$
$$= 2\int_{\kappa=0}^{\infty} e^{-\kappa^2\tau}\int_{m=\kappa-\frac{1}{2}}^{\infty}(2m+1)e^{-m(m+1)\sigma}\,dm\,d\kappa$$

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(5) Mulholland, *Proc. Cambridge Phil. Soc.*, 24, 280 (1928).

(6) Giauque and Overstreet, THIS JOURNAL, 54, 1731 (1932).

(7) Reiche and Rademacher, Z. *Physik*, 39, 444 (1926).

$$
\begin{aligned}
&= 2\int_0^\infty e^{-\kappa^2\tau}\,[(1/\sigma)\,e^{-(\kappa^2-1/4)\sigma}]\,\mathrm{d}\kappa \\
&= (2/\sigma)\,e^{\sigma/4}\int_0^\infty e^{-\kappa^2\rho}\,\mathrm{d}\kappa \\
&= \sqrt{\pi}\,e^{\sigma/4}/\sigma\,\sqrt{\rho} \\
&= \frac{\sqrt{\pi}}{\sigma\,\sqrt{\rho}}\,(1 + \sigma/4 + \ldots) \qquad (28)
\end{aligned}
$$

It is unlikely that the expansion in (28) is exactly correct beyond the first term. Using only this term, we obtain

$$H = 3RT/2 \qquad (29)$$

$$S = (R/2)\log\pi - R\log\sigma - (R/2)\log\tau + 3R/2 \qquad (30)$$

$$F/T = -(R/2)\log\tau + \mathrm{R}\log\sigma + (R/2)\log\tau \qquad (31)$$

For molecules with three different moments of inertia, it is not possible to express the energy levels by a formula; there is no real doubt, however, that for this case, to the same order of accuracy, it is merely necessary to replace a in (30) and (31) by $(\sigma_1\sigma_2)^{1/2}$.

The contribution from translation is given by the Sackur–Tetrode equation; at 1 atm. pressure

$$S = (5R/2)\log T + (3R/2)\log M - 2.300 \qquad (32)$$

$$S_{298} = 6.8625\log_{10} M + 26.000 \qquad (33)$$

$$F/T = 7.267 - (3R/2)\log M - (5R/2)\log T \qquad (34)$$

Actual molecules differ from the simple models we have so far considered because nuclei have spins and obey non-classical statistics. As a result, some rotational levels are actually not occupied, while others have quantum weights greater than those which we have assigned. For diatomic molecules these changes are relatively simple; thus for oxygen the even-numbered rotational levels are missing, while for hydrogen the odd-numbered levels (ortho-hydrogen) are relatively three times as abundant as the even. For polyatomic molecules, the changes are much more complex, and their determination is a matter of considerable difficulty. It is fortunate that for most purposes a much less detailed analysis will suffice; this comes about in the following way. Whenever it is permissible to replace the simple rotational Q-sum by an integral, the correct Q-sum, with an error only slightly larger, can be replaced by the same integral, with a numerical multiplier which gives the ratio of the actual number of rotational levels to the number for a simple rotator or top. At low temperatures this will no longer be permissible, and detailed calculations must be made. For room temperature and higher, however, it will always be a fair approximation to multiply the Q integral with a correction factor μ. Ludloff[8] has shown that this factor is the product of the spin multiplicities for the nuclei, divided by the number of equivalent rotational orientations for the molecule. For oxygen, this factor is just 1/2, since the O atom has no spin; for hydrogen it is $2^2/2 = 2$; for ammonia it is $3 \times 2^3/3 = 8$,

(8) Ludloff, *Z. Physik*, **67**, 227 (1929).

assuming a pyramid structure; for methane, tetrahedral, $2^4/12 = 4/3$; for acetylene, linear, $2^2/2 = 2$; ethylene, with a plane structure, $2^4/4 = 4$; ethane, probably $2^6/6 = 32/3$, though a more detailed analysis is desirable where bond rotation can occur.

In making calculations, it is conveninent to combine the contributions from translation, rotation and nuclear spin. We thus get the following formulas

Rotator

$$S = (7/2)R\log T + (3/2)R\log M + 175\ 375 + R\log J + R\log \mu \qquad (35)$$

$$S_{298} = (3/2)R\log M + R\log J + R\log \mu + 214.995 \qquad (36)$$

$$F/T = -(7/2)R\log T - (3/2)R\log M - R\log J - R\log \mu - 168.421 \qquad (37)$$

Top

$$S = 4R\log T + (3/2)R\log M + (1/2)R\log ABC + R\log \mu + 265.349 \qquad (38)$$

$$S_{298} = (3/2)R\log M + (1/2)R\log ABC + R\log \mu + 310.629 \qquad (39)$$

$$F/T = -4R\log T - (3/2)R\log M - (1/2)R\log ABC - R\log \mu - 257.401 \qquad (40)$$

Here J is the moment of inertia of the rotator, and A, B, C the three principal moments of the top. In using the formulas, R log, 10 is a conventional constant with the value 4.57500. Other physical constants are taken from "International Critical Tables."

Calculations

Methane is presumably a symmetrical tetrahedron, and should have all three moments of inertia equal. Actually Cooley[9] observed three different spacings in the three infra-red bands that he measured. It is uncertain how this result should be interpreted, as a molecule with two or three different moments of inertia would not lead to such a result. In the present calculations we shall use the value obtained from Raman spectra,[10] 5.17×10^{-40} g. cm.^{2}, which leads to a reasonable CH distance, and must certainly be almost correct.[10a]

Methane has nine modes of vibration, with four distinct frequencies. The first analysis was made by Dennison[11] who found two triple vibrations at 1304 cm.$^{-1}$ and 3014 cm.$^{-1}$, a double vibration at 1520 cm.$^{-1}$, and a single one at 4217 cm.$^{-1}$. The Raman observations of Dickinson, Dillon and Rasetti show clearly that 4217 cm.$^{-1}$ is a combination frequency, and that the fourth normal frequency is 2915 cm.$^{-1}$.[12] The vibrational analysis has been made in a different way by Mecke.[13] He used a treatment based on the concepts of valence and bending vibrations which is probably preferable to the central force analysis of Dennison. The result is that 1304 cm.$^{-1}$ becomes a double vibration and 1520 cm.$^{-2}$ a triple vibration;

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(9) Cooley, *Astrophys.* J., 62, 73 (1925).

(10) Dickinson, Dillon and Rasetti, Phys. *Rev.*, 34, 582 (1929).

(10a) Teller and Tisza, *Z. Physik*, 73, 791 (1932), have explained the variable spacings in the infra-red bands by rotation–vibration interaction, thus making the Raman moment of inertia still more likely.

(11) Dennison, *Astrophys.* J., 62, 84 (1925).

(12) Villars was apparently one of the first to adopt this change; New Orleans meeting, American Chemical Society, March, 1932.

(13) Mecke, Z. *physik. Chem.*, 17B, 1 (1932).

aside from this one point, there seems to be no doubt about the frequencies. We shall make the calculations using both the Dennison–Villars and the Mecke assignment.[14]

The thermal values necessary are known with quite sufficient accuracy in this case. The heat of combustion of graphite at 25° is 94,240 cal.,[15] and this value is unchanged when corrected to 18°. The heat of combustion of hydrogen[16] at 18° is 68,367 cal., and that of methane[17] is 212,946 cal. The heat content of graphite at 18° is 239 cal.;[18] the heat content of hydrogen at 18° is given by Giauque's[19] spectroscopic calculations as 1975 cal. The heat content of methane at 18° is calculated by (9) and (21) as 2335 cal. From these data the heat of formation of methane gas from hydrogen gas and β-graphite at the absolute zero is +16,174 cal.

The spectroscopic values of $(F^\circ - E_0^\circ)/T$ for hydrogen have been given by Giauque.[19] Values of this function for β-graphite have been computed by Clayton and Giauque[20] from specific heat data. An independent calculation, with a presumably different choice of specific heat equations, gave a maximum deviation of 0.009 cal./deg. up to 1500°K., rising to 0.039 at 3000°K. For the sake of uniformity, Clayton and Giauque's values are adopted here.

Table I gives the absolute value (including nuclear spin) of $(F^\circ - E_0^\circ)/T$ for methane, from spectroscopic data alone, and the values of $\Delta F/T$ and $\log_{10} K$ for its formation from the elements, based also on the foregoing heat of reaction. No entirely reliable equilibrium measurements are available. At the lower temperatures, it is very difficult to attain equilibrium with any catalyst, and there is also some uncertainty as to whether or not the effective solid phase is β-graphite. At the higher temperatures, hot carbon rods in non-isothermal systems have been used, and there is the possibility of perturbing reactions in the cooler parts of the systems. At the highest temperatures attained, there is clearly a very considerable formation of methane from acetylene in this way. Figure 1 shows the results of a number of workers; it is clear that the present calculations agree with the bulk of the data fairly well; the early work of Pring and his

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(14) Since this paper was written, it has been suggested by Ruedy [*Canada J. Research*, *7*, 328 (1932)] that the 1520 cm.$^{-1}$ frequency should be replaced by 1100 cm.$^{-1}$ Neither of these has been directly observed, and it is doubtful whether or not the change is desirable. If the change is made, methane becomes more stable at all temperatures, the effect increasing with the temperature; at 2000°K. the free energy of formation would be increased 2334 cal. and the equilibrium constant increased 80%; the agreement with experiment would be appreciably less good than at present.

(15) Roth and Naeser, *Z. Elektrochem.*, 31, 461 (1925); Giauque, THIS JOURNAL, 64, 2623 (1932). Since this paper was submitted for publication, Gordon and Barnes, *J. Phys. Chem.*, 36, 2601 (1932), have made spectroscopic calculations of the methane equilibrium up to 1200°K. They have used for the heat of combustion of graphite the older value 94,420 cal., and they have followed also the original Dennison assignment of frequencies.

(16) Rossini, *Bur. Standards J. Research*, *6*, *1* (1931).

(17) Rossini, *ibid.*, 6, 37 (1931).

(18) "International Critical Tables," Vol. V.

(19) Giauque, THIS JOURNAL, 62, 4816 (1930).

(20) Clayton and Giauque, *ibid.*, 64, 2610 (1932).

associates is surprisingly correct. With this assurance that there is no unsuspected gross error, it seems reasonable to assume that the calculated equilibrium constant is not in error by more than 25% up to the highest temperature given.

TABLE I

FREE ENERGY OF METHANE

	Dennison–Villars			Mecke
T	$-(F^\circ - E_0^\circ)/T$	$\Delta F/T$	$\log_{10} K$	$-(F^\circ - E_0^\circ)/T$
250	40.525	....	...	40.525
300	41.986	−40 879	8.935	41.982
350	43 232	−32.175	7 033	43.226
400	44.334	−25 529	5.580	44.323
450	45.325	−20 153	4.405	45.309
500	46.228	−15.956	3.488	46.205
550	47.073	−12 387	2.708	47.043
600	47.867	− 9 367	2.047	47.829
650	48.621	− 6 782	1.482	48 576
700	49.336	− 4 534	0.991	49.284
750	50.023	− 2.564	.560	49.963
800	50.686	− 0.821	.180	50 617
850	51.322	+ 0.732	− .160	51.247
900	51.949	+ 2.115	− .462	51.865
950	52 548	+ 3.369	− .736	52.458
1000	53.134	+ 4.504	− .985	53.037
1050	53 704	+ 5 536	−1.210	53.601
1100	54.258	+ 6.481	−1.417	54.150
1150	54.804	+ 7.344	−1.605	54.690
1200	55.336	+ 8.141	−1.779	55.217
1250	55.863	+ 8.870	−1.939	55.738
1300	56.373	+ 9.548	−2.087	56.243
1400	57.361	+10.767	−2.354	57.222
1500	58.316	+11.828	−2.585	58.168
1600	59.238	+12.763	−2.790	59.083
1700	60.132	+13.586	−2.970	59.970
1800	60.999	+14.313	−3.129	60.830
1900	61.831	+14.966	−3.271	61.656
2000	62.645	+15.542	−3.397	62.465
2100	63.431	+16.065	−3.511	63.246
2200	64.197	+16.542	−3.616	64.006
2300	64.937	+16.988	−3.713	64.743
2400	65.667	+17.390	−3.801	65.470
2500	66.371	+17.770	−3.884	66.170
2600	67.068	+18.115	−3.960	66.864
2700	67.730	+18.451	−4.033	67.521
2800	68.389	+18.750	−4.098	68.177
2900	69.031	+19.029	−4.159	68.815
3000	69.649	+19.296	−4.218	69.431
3500	72.568	....	...	72.339
4000	75.212	....	...	74.971
4500	77.589	....	...	77.342
5000	79.799	....	...	79.544

The tabular method of presenting free energy values, which has been used exclusively in Giauque's publications, does not appear to be entirely satisfactory; interpolation, even using third and fourth differences, is not accurate to 0.001 of a unit. Accurate values may be obtained by fitting an equation of the type

$$\Delta F/T = A/T + B + CT, \text{ or } \Delta F/T = A/T + B + C \log T$$

to three successive entries in the tables. The derivative of such an equation, preferably one of the second kind, will give a fairly satisfactory value of ΔH, the error in the worst cases being only about 50 cal.; the second derivative will give a very rough estimate of ΔC_p. The use of such a procedure would be very laborious in some cases, and it seems that an attempt should be made to give a single equation applicable over the entire range of temperature. It proves to be almost impossible to accomplish this with the usual form of equation. Closer consideration of the problem suggests that since $\Delta F/T$ is changing rapidly when T is small and slowly when it is large, a power series in T should not be expected to fit well; the inclusion of terms of the form $1/T^2$ and $1/T^3$, in addition to the usual $1/T$, leads to much better results. The most satisfactory equation which has been found for methane, with the Dennison–Villars choice of frequencies, is

$$\Delta F/T = -24{,}903.5/T + 1{,}763{,}748/T^2 - 1501 \times 10^5/T^3 - 0.4607 \log_{10} T - 9.194 \times 10^{-5}\, T + 29.2749 \qquad (41)$$

This equation reproduces the tabulated values with a maximum deviation of 0.026 in $\Delta F/T$, or 62 cal. in AF, or 1.3% in K. It has been made to give a value of ΔH_{291} correct within 6 cal., but at other temperatures the agreement is less good, the possible error being about 100 cal. It seems probable that more accurate A H values than this cannot be obtained from AF, and must be directly calculated when needed. A 5-constant equation only slightly less satisfactory than the preceding one is

$$\Delta F/T = -25{,}714.6/T + 2{,}041{,}540/T^2 - 1890 \times 10^5/T^3 - 1.5051 \log_{10} T + 32.8813 \qquad (42)$$

The maximum deviation in $\Delta F/T$ is 0.030, but ΔH_{291} is 160 cal. in error. This difference is probably due only in a small degree to the extra term in the former equation; (41) was fitted by least squares to $\Delta F/T$ at ten points and to A H at 291°, while the five constants of (42) were determined from only five values of $\Delta F/T$; it is this difference in procedure which is responsible for a large part of the superiority of (41).

Acetylene is undoubtedly a linear molecule; its moment of inertia is known very accurately as 23.509 g. cm^2.[21] A molecule of this type has three valence vibrations and two double bending vibrations. The original assignment of these vibrations, made by Mecke,[22] has been justly criticized by Olson and Kramers.[23] These authors pointed out that a simple treat-

(21) Levin and Meyer, *J. Opt. Soc.* Am., 16, 137 (1928).

(22) Mecke, Z *Physik*, 64, 173 (1930).

(23) Olson and Kramers, THIS JOURNAL, 54, 136 (1932).

ment gave for the ratio of the antisymmetric to the symmetric bending frequency the value $\delta_a/\delta_s = 0.816$, while Mecke's assignment, $\delta_s = 730$ cm.$^{-1}$, $\delta_a = 1326$ cm.$^{-1}$ gave $\delta_a/\delta_s = 1.88$; there was the further criticism that 730 cm.$^{-1}$ was observed in absorption, and hence should not be symmetric. Apparently, independently of this criticism, Mecke[24] has now revised his assignment. He puts $\delta_a = 729$ cm.$^{-1}$ and $\delta_s = 600$ cm.$^{-1}$. The former of these is observed in the infra-red, but the latter is not directly observed anywhere; it occurs in four combination frequencies, one of which is a difference combination, and one a triple combination. The ratio δ_a/δ_s is still somewhat out of line with Olson and Kramers' treatment, though less than before, and Mecke believes that the difference can be accounted for by more complete treatment of the coupling terms, such as he has given. It must be admitted, however, that this part of the assignment is not free from doubt. The valence vibrations are very probably given correctly; two of them, 1975 cm.$^{-1}$ and 3370 cm.$^{-1}$, are observed in the Raman spectrum; the third, 3277 cm.$^{-1}$, is observed in the infra-red, and should, on theoretical grounds, be very close to one of the Raman frequencies, both being essentially C–H vibrations. Since there seems to be no way of rearranging the observed frequencies more satisfactorily, we shall follow Mecke and take 1974 cm.$^{-1}$, 3277 cm.$^{-1}$, 3370 cm.$^{-1}$ and double vibrations at 600 cm.$^{-1}$ and 729 cm.$^{-1}$.

The uncertainty in the vibrational frequencies has at least the compensation that one is spared the pain of contaminating precise spectroscopic data by the inaccurate heat of combustion of acetylene. On the authority of Rossini[25] I have adopted 311,000 cal. in preference to 312,000 cal. given by the "International Critical Tables." It seems entirely possible that this value may be in error by as much as 2000 cal. The heat content of

TABLE II

FREE ENERGY VALUES FOR ACETYLENE

T	$-\dfrac{F^\circ - E_0^\circ}{T}$	$\dfrac{\Delta F^\circ}{T}$	$\log_{10} K$
300	42.809	166.445	−36.381
400	45.249	121.340	−26.522
500	47.320	94.310	−20.614
600	49.140	76.311	−16.680
700	50.776	63.470	−13.873
800	52.258	53.873	−11.776
900	53.626	46.425	−10.148
1000	54.893	40.485	− 8.849
1200	57.188	31.600	− 6.907
1500	60.182	22.773	− 4.978
2000	64.343	14.025	− 3.066
2500	67.784	8.848	− 1.934
3000	70.752	5.472	− 1.196

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(24) Mecke, *Z. physik. Chem.*, **17B**, 1 (1932).

(25) Private communication.

acetylene gas at 18° may be calculated to be 2331 cal.; with these figures and the thermal data given previously, ΔE_0° for the formation of acetylene is 54,275 cal.

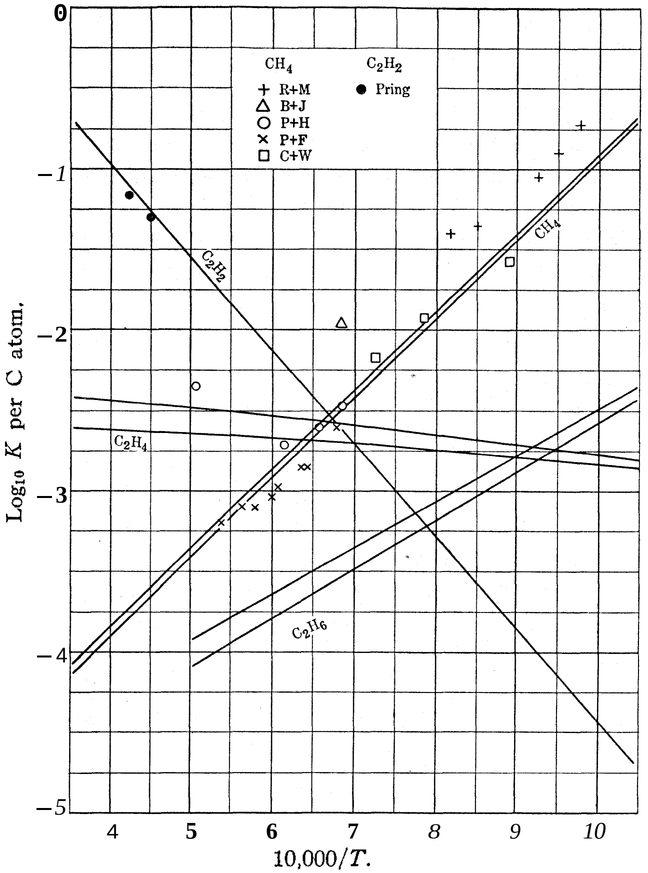

Fig. 1.—The curves give the calculated equilibrium constants, per gram atom of carbon, for the formation from hydrogen and β-graphite. For methane the upper curve is based on the Dennison–Villars frequencies, the lower curve on those of Mecke. For ethylene, the upper curve is based on 950 cm.$^{-1}$ for the torsional frequency, while the lower curve neglects this frequency. The curves for ethane are obtained by combining the two calculations for ethylene with the measured equilibrium constant for ethane dissociation.[26] The sources of the experimental equilibrium constants for methane are: R + M, Randall and Mohammad; B + J, Bone and Jerdan; P + H, Pring and Hutton; P + F, Pring and Fairlie; C + W, Coward and Wilson.[27]

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(26) Pease and Durgan, THIS JOURNAL, 60, 2715 (1928).

(27) Randall and Mohammad, *Ind. Eng. Chem.*, 21, 1048 (1929); Bone and Jerdan, *J. Chem. Soc.*, 71, 41 (1897); 79, 1042 (1901); Pring and Hutton, *ibid.*, 89, 1591 (1906); Pring and Fairlie, *ibid.*, 101, 91 (1912); Coward and Wilson, *ibid.*, 115, 1380 (1919).

The results for acetylene are given in Table II and shown in part in Fig. 1. For comparison, determinations by Pring[28] are plotted also. The close agreement is somewhat accidental, since the experiments from which these constants were obtained gave values much too high for methane and ethylene. One must assume that these latter gases were formed from acetylene in the colder parts of the apparatus.

The moments of inertia of ethylene are not known, but can be estimated in various ways. By assuming a C–C distance of 1.18 × 10^{-8} cm., C–H, 1.08 × 10^{-8} cm., and a tetrahedral valence angle for carbon, the moments may be calculated as 28.73, 23.69 and 5.03 × 10^{-40} g. cm.^{2}, giving a product of 3423 × 10^{-120}. Badger and Binder[29] interpreted their absorption measurements in the near infra-red in accordance with preliminary theoretical results of Nielsen. They give provisional values for the moments of 31, 27 and 3.8 × 10^{-40}, leading to a product of 3181 × 10^{-120}. Badger and Binder state, however, in a note added in proof, that the complete results of Nielsen[30] alter this interpretation somewhat, and lead to slight changes in the moments. In the present calculations the value 3423 × 10^{-120} will be used for the product of the three principal moments; this may well be in error by 25%. The resultant error in F/T would be 0.22 cal./deg.; the error in K would be only 12%. Our final values for ethylene will undoubtedly contain other errors of greater magnitude than this.

Ethylene has five valence vibrations, six bending vibrations and a torsional vibration about the double bond. Mecke[31] has assigned frequencies to all of these except the torsion. For ease in calculation we shall lump his eleven frequencies into five groups: a triple vibration at 950 cm.$^{-1}$, single at 1100 cm.$^{-1}$, double at 1400 cm.$^{-1}$, single at 1620 cm.$^{-1}$ and quadruple at 3090 cm.$^{-1}$. The resistance of the double bond to torsion is probably not great, but since the moment of the molecule about the C–C axis is small, the torsional frequency is presumably of moderate value.

TABLE III

FREE ENERGY VALUES FOR ETHYLENE

	Without torsional frequenc			With torsional frequency, 950 cm.$^{-1}$		
T	$-\frac{F^\circ - E_0^\circ}{T}$	$\frac{\Delta F}{T}$	$\log_{10} K$	$-\frac{F^\circ - E_0^\circ}{T}$	$\frac{AF}{T}$	$\log_{10} K$
300	49.085	42.487	−9.287	49.106	42.379	−9.263
500	53.652	31.748	−6.939	53.787	31.613	−6.910
700	57.206	27.969	−6.113	57.513	27.662	−6.046
1000	61.680	25.730	−5.624	62.279	25.141	−5.495
1500	67.854	24.478	−5.350	68.882	23.450	−5.126
2000	72.986	24.082	−5.264	74.390	22.678	−4.957
2500	77.394	23.948	−5.235	79.120	22.222	−4.857
3000	81.263	23.983	−5.242	83.271	21.975	−4.803

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(28) Pring, *J. Chem. Soc.*, *101*, 498 (1910).

(29) Badger and Binder, *Phys. Rev.*, 38, 1442 (1931).

(30) Nielsen, *Phys. Rev.*, 38, 1432 (1931).

(31) Mecke, *Z. physik. Chem.*, **17B**, 1 (1932).

We shall make computations both neglecting this frequency, and assigning it the value 950 cm.$^{-1}$. The true contribution is probably within these limits, though they may very well be too narrow to compensate for errors in the other frequencies.

We shall take the heat of combustion of ethylene at 18° to be 334,000 cal.; the heat content of the gas we calculate as 2414 cal. On this basis, the heat of formation of ethylene gas at the absolute zero is −10,800 cal.

The calculated values are given in Table III and shown in part in Fig. 1. There are no experimental data with which comparison is possible.

Some support for the frequencies assigned to ethylene, and hence to the foregoing calculations, is provided by recent specific heat measurements for ethylene gas from 0 to 70°.[32] The experimental results are represented by

$$C_p = 4.064 + 0.02022\ T$$

Table IV shows how the vibrational part of the specific heat compares with that calculated.

TABLE IV

VIBRATIONAL SPECIFIC HEAT OF ETHYLENE

Temp., °K.	Calcd. with torsion	Calcd. without torsion	Exptl.
300	2.349	1.901	2.182
350	3.567	2.925	3.193

It seems likely that with the rise of these spectroscopic methods, there will be a diminution of the importance of entropy in routine equilibrium calculations. We shall, however, give entropy values for these hydrocarbons. Our calculation of the absolute translational plus rotational entropy of methane at 25° gives 49.867 entropy units, in excellent agreement with 49.86 given by Giauque, Blue and Overstreet.[33] Upon adding the vibrational contribution, the total absolute entropy becomes either 49.974 or 49.955 entropy units for the Dennison–Villars and the Mecke frequencies, respectively. The agreement with the low-temperature specific heat value of 49.8 is good. For acetylene, the absolute translational plus rotational entropy is 49.359 at 25"; the vibrational contribution is 1.474, making a total of 50.833. For ethylene, the absolute translational plus rotational entropy is 56.903; the vibrational entropy is 0.452 or 0.569, the torsional frequency being omitted or taken as 950 cm.$^{-1}$; this gives a total of 57.355 or 57.472. For both acetylene and ethylene, the calculated values are probably in error by several tenths of an entropy unit.

It is planned to extend these calculations to other organic substances of scientific and technical interest. There appears to be some possibility of making orienting calculations even for the higher hydrocarbons.

(32) Haas and Stegeman, J. *Phys. Chem.*, *36*, 2127 (1932).

(33) Giauque, Blue and Overstreet, *Phys. Rev.*, 38, 196 (1931).

Summary

1. Methods have been given for the convenient calculation of free energies and entropies from spectroscopic data for polyatomic molecules.

2. Calculations have been made for methane, acetylene and ethylene.

3. The problem of representing the results of spectroscopic calculations by simple equations has been considered. It is shown that this can only be done satisfactorily by including in $\Delta F/T$ terms in $1/T^2$ and $1/T^3$.

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The Reactions of Atomic Hydrogen with Several Alkyl Halides

BY H. MARSHALL CHADWELL AND TOSHIZO TITANI[1]

The chemical behavior at ordinary temperatures of atomic hydrogen has been the subject of numerous investigations[2] during the past decade. The present investigation deals with the reactions of atomic hydrogen, produced by the Wood discharge tube, upon simple alkyl halide vapors: methyl fluoride, chloride, bromide and iodide, and ethyl chloride and bromide. The reactions with methane and ethane were also investigated. Boehm and Bonhoeffer[2] found that methyl chloride was attacked, but did not investigate the products. Of particular interest in connection with our results are the experiments of Hartel and Polanyi[3] on the reaction of sodium vapor with the alkyl halides.

Our experiments have shown that the reactions concerned are complicated, that in the series methyl fluoride, chloride, bromide and iodide, the amount decomposed under the experimental conditions varies from 0 to 100%. Both methyl and ethyl halides form methane, ethane and a small amount of ethylene. The chlorides produce only hydrogen chloride, while the bromides and iodides yield both hydrogen halide and free halogen.

Experimental Manipulation

Purification of Materials

Methyl Fluoride.—The methyl fluoride was prepared by the method of Moissan[4]

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[2] For a review of the early literature see Bonhoeffer, *Ergebnisse Exakten Naturwissenschaften*, 6, 201 (1927), and Taylor, THIS JOURNAL, 48, 2840 (1926). For reactions with hydrogen produced by the Wood discharge tube, Bonhoeffer and Boehm, Z. *physik. Chem.*, 119, 385 (1926); Bonhoeffer and Harteck, *ibid.*, 139, 64 (1928); Wartenberg and Schultze, *ibid.*, B2, 1 (1929); Urey and Lavin, THIS JOURNAL, **51**, 3286,3290 (1929); Geib and Harteck, Z. *physik. Chem., Bodenstein Festband*, 849 (1931); Dixon, THIS JOURNAL, **54**, 4262 (1932). See also Smallwood, ibid., 61, 1985 (1929); Bichowsky and Copeland, *ibid.*, **50**, 1315 (1928); Harteck, Z. *Bhysik. Chem.*, **139**, 98 (1928).

[3] Hartel and Polanyi, Z. *Bhysik. Chem.*, **B11**, *97* (1931).

[4] Moissan, *Jahresber. Chem.*, 41, 931 (1888).

from methyl iodide and silver fluoride[5] in an evacuated all-glass apparatus, the methyl fluoride being condensed with liquid air and subsequently fractionally distilled.

Methyl Chloride, Bromide and Iodide. Ethyl Chloride and Bromide.—These alkyl halides were obtained from a reliable commercial source and purified (in vacuum). by passing the vapor over fresh calcium oxide, followed by very careful fractional distillation. Blank experiments proved the absence of free halogen or halogen acid.

Methane.—Methane, obtained in a cylinder from a commercial source, was condensed with liquid air, and twice fractionally distilled, the final middle fraction being used in the experiments.

Ethane.—Ethane was prepared by the action of a copper–zinc pair on ethyl iodide, the gas being washed with water, fuming sulfuric acid. concentrated potassium hydroxide, and finally condensed with liquid air. It was then fractionally distilled three times, any methane being removed by pumping.

Apparatus

The atomic hydrogen was produced in a discharge tube similar in design to that used by Geib and Harteck.[6] Figure 1 shows the assembly of the apparatus.

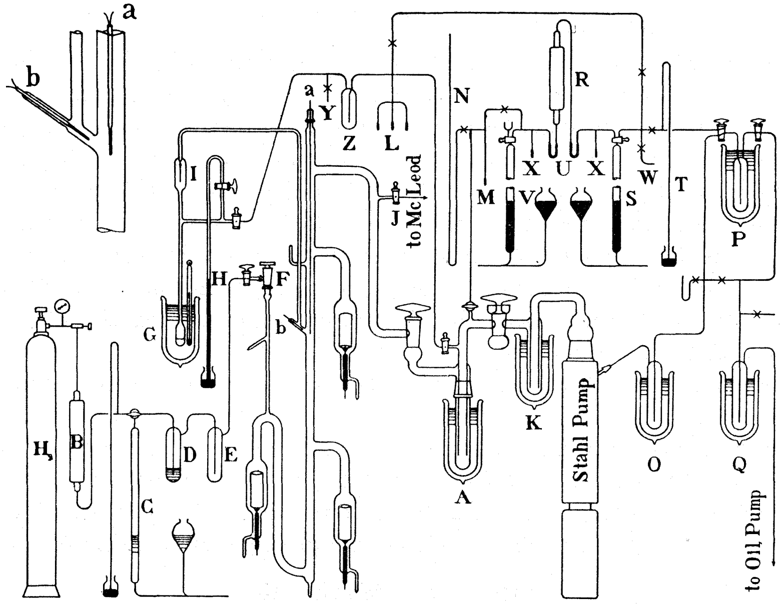

Fig. 1.—Diagram of apparatus.

The pumping system consisted of a large all-metallic three-stage mercury vapor Gaede pump electrically heated, with a rotary oil pump producing the forevacuum. A linear velocity of hydrogen of 7 meters per second was obtained when the hydrogen was admitted at the rate of 50 cc. (atmospheric conditions) per minute. The pressure of hydrogen in the apparatus was about 0.3 mm.

Electrolytic hydrogen from a cylinder, purified by heated platinized asbestos, was saturated with water vapor in the trap (D) or dried when desired by placing liquid air

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(5) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Band V, Abt. 2, 87 (1914).

(6) Geib and Harteck, Z. *physik Chem., Bodenstein Festband,* 849 *(1931).*

about the second trap (E). The rate of flow measured by the buret (C) was controlled by a very fine metallic needle valve (F).

The alkyl halide, stored as a liquid in a bulb sealed to the apparatus at (G), was introduced in various amounts by surrounding (G) with baths of different temperatures, the resulting vapor pressures being read on the manometer (H). The vapor then passed through the fine capillary (I). Blank experiments established the velocity of halide (moles per minute) for different vapor pressures.

In all of the experiments reported the alkyl halide entered the hydrogen from the discharge tube through the lower side tube (30 cm. above the discharge). That no diffusion of vapor into the discharge took place was predicted from a calculation of this hack-diffusion, and proved experimentally by no spectroscopic change in the discharge. A transformer delivering approximately 3000 volts and producing a current of 300 m.a. was used to excite the discharge. Two copper-constantan thermocouples inclosed in small glass tubes were mounted within the reaction zone as shown in Fig. 1. This section of the vertical tube was surrounded by a mantle and cooled by a blast of air.

The products of the reactions passed through the large trap (A) immersed in liquid air. The second large trap (K), also cooled by liquid air, prevented the diffusion of mercury vapor from the pump. Materials caught in the first trap could be fractionally distilled, either into one of the small tubes (L) for subsequent weighing and analysis or into the tube (M) for vapor pressure measurements with the manometer (N), or could be removed directly for analysis.

Method of Analyzing the Hydrocarbons

Because of the relatively small partial pressures of methane, ethane and ethylene, and possibly acetylene, in the gas mixture, all of these gases passed through the traps (A) and (K). They were caught by activated coconut charcoal, cooled with liquid air, before the gas passed to the oil pump.

The gases leaving the mercury-vapor pump passed through a trap (O), cooled to $-80°$ and then through the tube of charcoal (P). The oil pump, protected by its liquid-air trap (Q), could be used independently of the charcoal by a suitable manipulation of the stopcocks, as is evident from Fig. 1. This use of charcoal proved very effective in holding the hydrocarbons and in decreasing the amount of hydrogen in the gas mixture. After an experiment the contents of the charcoal tube were pumped into the copper oxide tube (R) by means of the leveling bulb (filled with mercury) connected to the first buret (S). Here the remaining hydrogen was burned at 240" by circulating the gas over the copper oxide by means of the leveling bulbs and burets (V) and (S). The small traps (U), cooled with liquid air, were attached to both ends of the copper oxide tube to condense ethane, ethylene, acetylene, most of the methane and water.

The methane, contaminated with a small amount of inert gas which was probably oxygen from the decomposition of water in the discharge tube, was pumped out of the apparatus, by means of buret (S) and its leveling bulb, into a buret connected at (W). This gas was analyzed by combustion with oxygen and usually showed 95% methane.

The higher hydrocarbons, carbon dioxide and water, were distilled from the traps (U) into one of the small tubes (X), cooled with liquid air, sealed off and analyzed. The gas in the tube (X) was collected over mercury in a 25-cc. buret by breaking its capillary end in an evacuated rubber tube connected to the buret. During this operation the tube was cooled to $-20°$, so that the water remained as ice. The volume of gas remaining in the tube was later measured and a correction applied. The gas in the buret was analyzed for carbon dioxide by absorption with potassium hydroxide, for acetylene with alkaline mercuric cyanide,[7] for ethylene with half-saturated bromine water followed by potassium hydroxide, and for ethane by combustion with oxygen. The total quan-

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(7) Treadwell, *Helv. Chim. Acta*, **2**, 60 (1919).

tity of hydrocarbon found agreed very well with that calculated from the extent of the reaction as determined by the amount of inorganic substances produced.

Method of Analysis for Halogen and Halogen Hydride

The extent of the reaction (percentage decomposed) could be determined by two methods: first, the relation of unreacted halide to the amount entering the apparatus, and, second, the amount of free halogen and halogen hydride formed. It was found that both methods gave the same reproducible results.

Fluoride.—No measurable reaction took place with methyl fluoride.

Chlorides.—No free halogen was found. Because of its relatively high vapor pressure, hydrogen chloride could not be caught quantitatively in Trap A, either by a frozen layer of water, of ammonia hydroxide, or potassium hydroxide solution, or by solid potassium hydroxide. Consequently the percentage of methyl and ethyl chlorides decomposed was obtained by distilling at −50° the unreacted halide from Trap A into a small tube (L, Fig. 1), sealing and weighing. Vapor pressure measurements showed the material to be pure halide

Bromides.—Bromine and hydrogen bromide were products of the reaction of the alkyl bromides with atomic hydrogen, and were caught in Trap A. The unreacted alkyl halide was distilled from Trap A (ethyl bromide at −40°, methyl bromide at −60°, for four to five hours), into a small tube (L). This was weighed and analyzed for the trace of hydrogen bromide and bromine which it contained. The residue in Trap A was also analyzed for bromine by titrating with 0.01 N sodium thiosulfate and for total bromide with 0.01 N silver nitrate after heating with dilute ammonium hydroxide.[8] Knowing the velocity of the entering alkyl halide, the percentage which reacted could be calculated from the unreacted alkyl halide and from the inorganic products formed.

Iodide.—The reaction of ethyl iodide with atomic hydrogen was not studied because of the relative ease of thermal decomposition. With methyl iodide, both hydrogen iodide and free iodine were obtained. No unreacted methyl iodide could be found, showing complete reaction of the alkyl halide.

The content of Trap A was analyzed by repeatedly extracting with small amounts of chloroform, titrating the water layer with 0.01 N sodium hydroxide and the chloroform layer with 0.01 N sodium thiosulfate in the presence of potassium iodide and starch."

The Concentration of Atomic Hydrogen

The concentration of atomic hydrogen, present in the reaction zone under conditions similar to those before the alkyl halide was admitted, was measured by the method of Wrede and of Harteck[10] with the modification of substituting for the fine capillary a sintered glass plug, similar to that used by Dr. W. G. Leighton.[11] The results are given in Table I.

TABLE I

CONCENTRATION OF ATOMIC HYDROGEN

Per cent. H at different currents (m. a.) and velocities of H_2 (cc./min.)

Current Velocity	100	100	200	200	300
50	44	48	52	55	56
60	50	58	64	68	70

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[8] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, New York, fourth ed., Vol. II, p. 324.

(9) Beckmann, Ann., 367, 289 (1909).

[10] Harteck, Z. *physik.* Chem., 139, 98 (1928); Wrede, Z. *Instrumentenk.*, 48, 201 (1928); Geib and Harteck, *Z.* physik. Chem., Bodenstein *Festband*, 849 (1931).

[11] Leighton, unpublished investigation. This method is being confirmed in this Laboratory by Dr. H. Cordes. We are indebted to Dr. Cordes for calibrating the Wrede gage and for suggestions concerning the mechanism of the reactions.

Experimental Results

Light and Heat Produced by the Reactions.—The production of a yellowish-green light by the reaction of atomic hydrogen with organic compounds has been reported by many investigators.[12] We have observed this same light in the reactions with the alkyl bromides, stronger in the case of the methyl compound than with the ethyl.

The reactions produced a considerable quantity of heat, the position of maximum heating being very dependent upon the velocity of the alkyl halide entering the stream of hydrogen. In all cases the highest temperatures were obtained in the experiments with the greatest amount of alkyl halide. These temperatures were: for methyl chloride 105° (RX/H = 0.122), ethyl chloride 125" (RX/H = 0.135), methyl bromide 135° (RX/H = 0.058), ethyl bromide 140° (RX/H = 0.113), methyl iodide 125" (RX/H = 0.043). It is highly improbable that these results represent accurately the maximum temperature existing in the reaction zone. From the measurements of temperature with the two thermocouples, it could be concluded that the length of the reaction zone in the tube was greater for methyl chloride than for methyl bromide, which in turn was greater than for methyl iodide. In the case of the methyl chloride not all of the atomic hydrogen was used up by the reactions.

Since methyl iodide was the most easily decomposed by heat of any of our materials, we made blank experiments with a heating jacket about the reaction zone, and using only molecular hydrogen. No halide decomposed at 295°. We therefore concluded that it was improbable that thermal reactions taking place on the walls played a part in determining the products of the reactions.

Hydrocarbon Products.—The results of the examination of the hydrocarbon products of the reactions are given in Table II.

TABLE II

HYDROCARBON PRODUCTS

Velocity of hydrogen 50 cc./min. Current through discharge 300 m.a.

Expt.		Time, min.	Vel. RX mole, $\times 10^6$/min.	RX/H	CH4	Volume (cc.) of gas found					CH₄ equiv., cc.		% RX found as		
						CO_2	C_2H_2	C_2H_4	C_2H_6	C_2H_x	Found	Calcd.	CH_4	C_2H_x	CO_2
CH_3Cl	A	60	140	0.086	9.0	9.0				50.5	19	18	50	$\leqq 6$	50
	B	140	74	.046	13.5	20.5				50.3	34	25	54	$\leqq 2$	82
CH_3Br	A	80	87	.054	33.8	14.4	0.5	3.0	7.0	10.5	69	63	54	33	23
CH_3I	A	40	70	.043	32.6	6.8	0.3	1.2	6.6	8.1	56	67	49	24	10
	B	30	64	.040	21.8	9.5				6.9	45	46	47	30	21
	C	30	65	.040		4.8	0.2	0.7	6.5	7.4		47		32	10
	D	60	29	,018	25.1	14.2				5.8	51	42	60	28	34
	E	60	29	.018	25.8	4.2				5.0	40	42	61	24	10
C_2H_5Cl	A	60	148	.091	47.0	15.2	0.5	1.5	4.6	6.6	75	81	58	16	19
	B	60	148	.091	44.5	19.9	0.7	2.1	4.3	7.1	79.	81	55	18	25
C_2H_5Br	A	80	113	.070	55.0	16.9	1.2	9.2	21.0	31.4	138	134	43	47	13
	B	40	114	.070		3.2	0.9	5.3	9.9	16.1		74		44	4

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(12) See, for example, Bonhoefferand Harteck, Z. *physik.* Chem., **139**, 64 (1928).

The table is self-explanatory. All ratios of concentrations are molal. The theoretical yield (cc. CH4 or its equivalent) was calculated from the percentage decomposition determined from the inorganic products (next section), with the exception of the bromides, where the bromine and hydrogen bromide formed were titrated directly. In experiments CH_3I C and C_2H_5Br B, the copper oxide was not used.

When the difficulties of the analyses are considered, for instance in experiment CH_3Cl B the products from 25 cc. of reacted alkyl halide had to be found in 7000 cc. of hydrogen, the results are satisfactory.

An examination of the table shows that both methyl and ethyl halides produced methane, ethane, and perhaps a trace of ethylene. The composition of the hydrocarbon product was not very dependent upon the relative concentration of atomic hydrogen. At the same relative concentration of alkyl halide to atomic hydrogen, the different methyl halides produced the same quantity of methane. Methyl chloride produced practically no ethane, while the bromide and iodide gave the same amount. With an increase of atomic hydrogen concentration, the concentration of methane increased. Ethyl bromide produced less methane and more ethane than did ethyl chloride.

If any hydrocarbons of greater molecular weight than ethane, or any quantity of acetylene, were produced, they would have been caught in Trap A. No evidence, either from distillation and subsequent vapor pressure measurements or from analysis, could be obtained for such products.

The continual formation of such a relatively large quantity of carbon dioxide was rather surprising. Blank experiments proved that only small quantities could have resulted from oxidation of hydrocarbon by the copper oxide or from oxidation in the tube of absorbent charcoal. We consequently concluded that at least the major portion of carbon dioxide arose from a reaction above the discharge tube between either O or OH, formed by the presence of water vapor and alkyl halide or hydrocarbon. These reactions must have produced carbon monoxide which was subsequently oxidized. This conclusion is supported by the fact that the amount of carbon dioxide found is very dependent upon the duration of the experiment, about 0.16 cc. being formed each minute for methyl compounds, and 0.26 cc./min. for ethyl compounds. Harteck and Kopsch[13] have shown that atomic oxygen produced in a discharge tube from oxygen gas reacts very slightly (0–2%) with methane, but to a greater extent (2–5%) with ethane and alkyl halides. In our experiments, the greater velocity of oxidation of ethane (than methane) would have resulted in a relatively larger change in the ethane concentration, because the ethane was present in smaller quantities. Consequently the methane concentration found

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(13) **Harteck and Kopsch,** *Z. physik. Chem.*, **B12, 327 (1931).**

more nearly represents that produced by the reaction of atomic hydrogen on the alkyl halide.

In order better to understand the mechanism of these reactions, experiments on the reaction of atomic hydrogen with methane and ethane were also performed. With methane no reaction could be obtained, confirming the observations of previous investigators. Two experiments with ethane were made. In the first (25 cc. of ethane was used), 5% of the ethane was found as methane, 1.4% as carbon dioxide and 1.6% as ethylene; in the second (150 cc. ethane), 3% of the ethane as methane, 3% as carbon dioxide and 1.7% as ethylene. No acetylene or higher hydrocarbons were obtained. The heat generated by the reaction (or catalysis of recombination of atomic hydrogen) was large.[14] We concluded that the greater portion of the methane produced from the alkyl halides under our conditions was not formed by intermediate ethane.

Inorganic Products and Extent of the Reaction of the Alkyl Halides with Atomic Hydrogen.—When methyl fluoride was introduced into the stream of atomic hydrogen, no heating effect could be observed and no etching of the glass by hydrogen fluoride formed by the reaction could be seen. Consequently we concluded that there was no reaction.

The results for the chlorides, bromides and iodide are given in Tables III, IV and V. The percentages of alkyl halide decomposed at different

TABLE III

METHYL AND ETHYL CHLORIDE

Velocity of hydrogen 50 cc./min. Current through discharge 300 m. a.

No.	Time. min.	Moles RX X 10^6 Put in	Unreacted	Reacted	RX/H	% RX Reacted
			Methyl Chloride			
1	40	2700	2440	260	0.042	9.6
2	20	3940	3625	315	.122	8.0
3	40	1044	954	90	.016	8.6
4	40	1444	1297	147	.022	10.2
5	60	1566	1414	152	.016	9.7
			Ethyl Chloride			
1	40	2230	1410	820	0.034	37
2	40	1188	724	464	.018	39
3	20	4392	3760	632	.135	14
4	20	1439	970	469	.044	33
5	60	1581	986	595	.016	38
6	40	1424	884	540	.022	38
7	40	1074	687	387	.016	36
8	40	1205	792	413	.019	34

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(14) Wartenberg and Sehultze, Ref. 2, concluded that ethane largely catalyzed the recombination of atomic hydrogen while Bonhoeffer and Harteck, Ref. 2, found that about 25% of the ethane reacted Under their experimental conditions 480 cc. of gas was condensed in the liquid-air trap, from 640 cc. of ethane introduced. They concluded that the loss (25%) was probably methane and ethylene. The difference between their results and ours may have been caused by a loss of ethane passing through their liquid-air trap or by a difference in relative concentrations.

TABLE IV

METHYL AND ETHYL BROMIDES

Current through the discharge 300 m.a. for methyl bromide, 250 m.a. for ethyl bromide

		Vel.	Moles RX × 10^6			G. equiv. × 10^6				% RX reacted	
No.	Time, min.	H_2, cc./min.	Put in	Unreacted	Reacted	Br	HBr	HBr/Br	RX/H	RX	Br + HBr
					Methyl Bromide						
1	40	60	916	295	621	24	619	26	0.009	68	70
2	40	60	3096	1811	1285	99	1139	12	.029	42	40
3	40	50	3744			65	1096	17	.058		31
4	40	50	1384	620	764	48	726	15	.021	55	56
5	40	50	921	295	626	29	571	19	.014	68	62
					Ethyl Bromide						
1	40	39	1320	690	630	39	648	17	0.039[b]	48	52
2	20	60	2202	1376	826	75	752	10	.043	37	38
3	40	51	1290			28	778	28	.020		63
4	30	50	5350	4400	950	62	936	15	.113	18	19
5	30	50	1635	872	763	45	690	15	.035	47	45
6[a]	40	50	920	250	670	24	616	26	.014	73	70

[a] Current through discharge 300 m.a. [b] Calculated from a value for the % atomic hydrogen obtained by extrapolating the data in Table I.

TABLE V

METHYL IODIDE

Velocity of hydrogen 50 cc./min. Current through discharge 300 m.a.

		Moles RX × 10^6	G. equiv. × 10^6				% RX
No.	Time	put in	I	HI	HI/I	RX/H	reacted
1	20	1386	300	1020	3.4	0.043	95
2	20	612	63	529	8.4	.019	97
3	10	462	110	360	3.3	.029	102
4	10	449	85	358	4.2	.028	99
5	10	372	40	334	8.4	.023	101
6	10	478	115	362	3.2	.030	100
7	10	332	28	311	11.0	.021	102
8	10	676	210	457	2.2	.042	99
9	20	364	21	351	16.7	.011	104
10	10	346	40	317	7.9	.021	103

values of the ratio RX/H are plotted in Fig. 2. It should be noted that the curve for ethyl bromide was determined not only by varying the amount of alkyl halide introduced, but also by varying the concentration of atomic hydrogen.

An examination of the data for the methyl halides shows that the percentage of halide reacted varied from 0 to 100 (from fluoride to iodide). The extent of the reaction of ethyl bromide was about the same as that of methyl bromide, but the behavior of ethyl chloride was quite different from that of the methyl compound. The methyl chloride was little affected by a change in the relative concentration of atomic hydrogen. The gradual sequence in the order of the methyl halides suggests a change in the heats of activation from a low value for the iodide to such a large value for the fluoride that no perceptible reaction took place.

Figure 3 shows the variation of the relative amounts of hydrogen halide

(HX) and free halogen (X) produced by different concentrations of atomic hydrogen. As the concentration of atomic hydrogen increased, the relative amount of hydrogen bromide and iodide increased. Ethyl bromide produced more hydrogen bromide than did methyl bromide, for a given ratio of RX/H. And, finally, the products of the reaction of methyl iodide were richest in free halogen.

From the experiments of Boehm and Bonhoeffer on the action of atomic hydrogen on bromine, we can conclude that the quantity of bromine changed to hydrogen bromide decreased with an increase in the value of Br_2/H. The shape of the curve, when HBr/Br_2 is plotted against Br_2/H, is the same as when HX/X is plotted against CH_3X/H. This dependence of HX/X upon CH_3X/H is believed to be the result of the action of atomic hydrogen upon the hydrogen halide and halogen formed during the decomposition of CH_3X and producing a condition of equilibrium. As a consequence, Fig. 3 cannot be used in deciding whether free halogen or hydrogen halide is the product of the primary reaction.

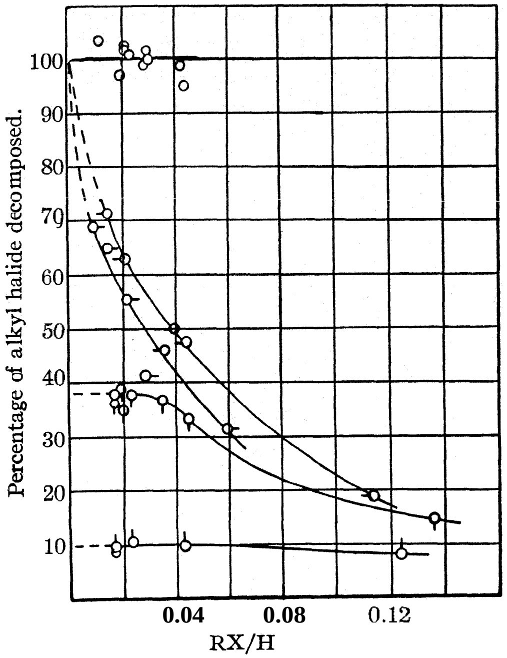

Fig. 2.—The percentage of alkyl halide decomposed by atomic hydrogen. The molar percentages of alkyl halide are plotted as ordinates, the values of the ratio RX/H as abscissas. The data for methyl chloride are represented by ⫰, for ethyl chloride by ⫯, for methyl bromide by O–, and for ethyl bromide by –O. Methyl iodide was completely decomposed at all values of RX/H investigated Methyl fluoride did not react.

Discussion of Results

Because of the relatively small probability of three-body collisions, and because of the experimental fact that our reactions took place in a very limited space, we believe that the primary reactions which occurred were due to two-body collisions.

There are three possible primary reactions to explain the results for methyl halides.

$$\text{(I)} \quad CH_3X + H = CH_3 + HX$$
$$\text{(II)} \quad CH_3X + H = CH_4 + X$$
$$\text{(III)} \quad CH_3X + H = CH_2X + H_2$$

The heats of reaction[15] (kilogram calories per gram mole) for these three changes and for the different methyl halides are given in Table VI.

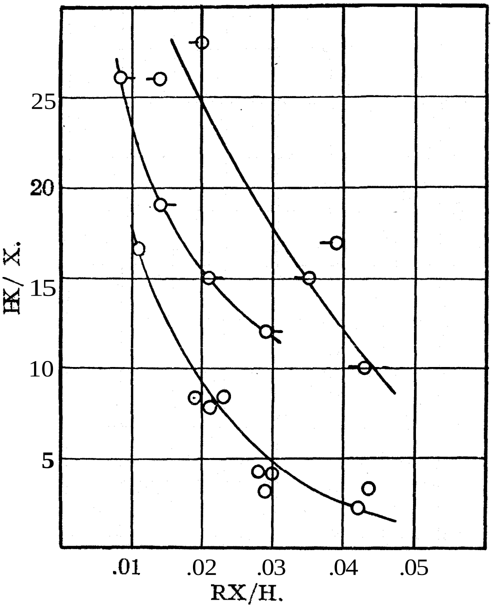

Fig. 3.—The relative concentrations of hydrogen halide to free halogen found in the reaction products. The values of the ratio of the gram equivalents of hydrogen halide (HX) to free halogen (X) are plotted as ordinates, while the values of RX/H are plotted as abscissas. The data for methyl iodide are represented by O, those for methyl bromide by O-, and those for ethyl bromide by -O. The alkyl chlorides produced only hydrogen chloride.

A reaction similar to I has been used by Hartel and Polanyi[3] to explain the reaction of sodium vapor upon the methyl halides. They have concluded from their experimental results as well as from theoretical considerations that the heats of activation (kg. cal.) increase from methyl iodide to methyl fluoride ($CH_3I = 0$, $CH_3Br = 3.2$, $CH_3Cl = 8.8$, $CH_3F = 25$). From the similarity of the reactions we can suppose that reaction I is the primary reaction and, furthermore, because of the comparable values of the H–X and Na–X bonds (H–Cl = 101 kg. cal., Na–Cl = 96, H–Br = 85, Na–Br = 89, H–I = 67, Na–I = 72), it is safe to conclude that the heats of activation for our reactions are of the same order of magnitude as those for the reactions with sodium vapor.

That reaction II is the only primary reaction is very improbable. First, this reaction cannot come into the consideration of the chlorine compound because we know from photochemical data[16] that methane reacts with chlorine atoms, formed from molecular chlorine by

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(15) The heats of reaction were calculated from the following data: $^1/_2(H_2) + {}^1/_2(X_2) = (HX) + a$, $X + X = (X_2) + b$, heats of combustion of $CH_3X = c$.

X =	H	F	Cl	Br	I
a		64 2"	21.9"	12 3[c]	1.4[a,d]
b	101 9[a]	64 6"	56 9[a]	45 2[a]	35 4[a]
c	212 8[e]		164.8[e]	184 7[e]	201 3[e]

[a] Landolt-Bbrnstein, "Physikalisch-chemische Tabellen," Second Supplement, 1931, pp 1498, 1615. [b] Wartenberg and Hanisch, *Z. physik. Chem..* **A161**, 463 (1932). [c] Gmelin, "Handbuch der anorg. Chem ," 7, 191 (1931) [d] $[I] = (I) - 7\ 5$ kg cal., Gmelin, *ibid* , 8, 81 (1931). [e] Landolt-Bornstein, Vol. II, 1923, or Second Supplement, 1931. The data for CH_3F were calculated from the above, together with $CH_3F + H_2 = CH_4 + HF + 20\ 0$; Grimm, "Handbuch der Physik," 24, 536 (1927). The values for the binding forces (kg. cal.) are C–H = 92, C–F = 118, C–Cl = 71, C–Br = 58, C–I = 44. See Hartel and Polanyi, Ref 3.

(16) Coehn and Cordes. Z. *physik. Chem.*, **B9**, 1 (1930).

TABLE VI

HEATS OF REACTION

Alkyl halide	Heat of reaction (cal.) for reaction number I	II	III
CH_3F	30	−26	10
CH_3Cl	30	21	10
CH_3Br	28	34	10
CH_3I	27	48	10

the action of suitable light; to form methyl chloride and hydrogen chloride. Second, the formation of ethane is not possible since methane is not reacted upon by atomic hydrogen. Further, it is certain that methane cannot react with any of the possible intermediate products of our reactions with the exception of atomic chlorine.

That reaction III is the primary reaction is also improbable. It is evident from our experimental results that the reaction of methyl fluoride involves a large heat of activation, and that as we proceed through the series to the iodide, the heat of activation must decrease. If III was the primary reaction, similar rather than very different heats of activation would be expected, because the primary process, according to this mechanism, is the same for all the methyl halides, namely, the removal of a hydrogen atom from the methyl group by a free hydrogen atom. From a study of band spectra[17] it has been concluded that the distances between the carbon and hydrogen atoms in the different methyl halides are practically the same. Consequently we can believe that the strength of the C–H bond is not very greatly affected by the change of halogen. Very different heats of activation for the different methyl halides are quite improbable.

The constant relationship between the amount of methane formed to the amount of methyl halide reacted, in the case of all of the methyl halides, makes it improbable that two of the three or all three reactions take place concurrently and to a similar extent for the different halides. The results of our experiments can all be explained by assuming that only reaction I is the primary process. That the other reactions take place to a very small degree cannot be excluded because of possible experimental error.

In the reaction of methyl chloride a maximum amount of 10% of the material reacted. This amount was not appreciably increased by an increase of atomic hydrogen concentration. It is possible that a portion of this decomposition of halide was due to oxidation by either O or OH formed in the discharge tube. This oxidation process could not change the character of the curve, because it was taking place to the same degree in all of the experiments.

To explain the experimental facts for all of the methyl halides, we must consider the following reactions

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(17) Mecke, Leipziger Vortrage, "Molekulstruktur." 1931.

$$CH_3X + H = CH_3 + HX \quad (1)$$
$$HX + H = H_2 + X \quad (2)$$
$$CH_3 + HX = CH_4 + X \quad (3)$$
$$CH_3 + HX + H = CH_3X + H_2 \quad (4)$$
$$CH_3 + H + M = CH_4 + M \quad (5)$$
$$CH_3 + X + M = CH_3X + M \quad (6)$$
$$H + X + M = HX + M \quad (7)$$
$$X + X + M = X_2 + M \quad (8)$$
$$CH_3 + CH_3 + M = C_2H_6 + M \quad (9)$$

M represents a third body or the wall. From the photochemical investigation[16] of the chlorination of methane we know that reaction **3** is very improbable in the case of methyl chloride. Free methyl (CH_3) formed by 1 can react according to 4 and 5, and to a lesser degree according to 6 and 9. The reactions 4 and 6 produce a reformation of methyl halide. The fact that a maximum value of 10% of methyl chloride reacted, not increasing with an increase of atomic hydrogen concentration, must be explained by such a mechanism leading to the reformation of the alkyl halide. The small value for this decomposition is quite understandable when the relatively high heat of activation is considered. From previous experiments by Boehm and Bonhoeffer we know that the hydrogen halides act as catalysts for the recombination of atomic hydrogen according to the mechanism of reaction 2 and 8 followed by the reaction $X_2 + H = HX + X$.

In the case of methyl bromide and iodide reaction **3** must be considered. It takes place with reaction 2 in the formation of free halogen. That we found free bromine and iodine, but no free chlorine, is also in accord with Boehm and Bonhoeffer's experiments with the hydrogen halides. The reformation of these methyl halides, taking place by reactions 4 and 6, both three-body collisions, must be slower than the formation of methane by the two-body collision-reaction **3.** Furthermore, these reactions (4 and 6) must increase more rapidly than linearly with the CH_3 concentration. Consequently the percentage of methyl bromide found decomposed decreased when its concentration was increased.

The relatively high concentration of methane is to be expected from the above mechanism. Because ethane was obtained in a considerable amount, one can assume perhaps that the life period of the CH_3 radical is sufficiently great so that the number of successful three-body collisions, according to reaction 9, is comparable to the number of collisions which produce methane.

The constant quantity of methane produced by the bromide and iodide is understood since the two-body reaction **3** takes place more rapidly than reactions 4, 5, 6 and 9, all three-body reactions which remove CH_3. In order to explain the same amount of methane from methyl chloride, one must make the further assumption that reaction 5 is much faster than reaction 6. This is plausible because the concentration of atomic hydrogen must have been much greater than that of chlorine.

Any suggested reaction mechanism for the decomposition of ethyl bromide and iodide is very complex and uncertain. If we accept the following values for the energies of binding (kg. cal.) namely, C–C[18] = 71, C–H = 92, C–Cl = 71, C–Br = 58, we should conclude that the C–Br bond is more easily attacked than the C–Cl bond and that the C–H bond is probably not attacked at all. The attack of hydrogen atoms on the C–C linkage would produce methane and should be about the same in the case of bromide as of chloride. Therefore the relative quantity of ethane to methane should be greater for ethyl bromide than for ethyl chloride, which is in accordance with the experimental facts.

We wish to thank Professor K. F. Bonhoeffer, Director of the Institute of Physical Chemistry of the University of Frankfort, for making available to us the facilities of the Institute, and for his kindly interest in this investigation.

Summary

The reactions of atomic hydrogen, produced by a Wood discharge tube, on methyl fluoride, chloride, bromide, iodide and ethyl chloride and bromide have been investigated. Incidental experiments were also made with methane and ethane.

The organic and inorganic products of the reactions have been determined quantitatively. This required the development of a method for analyzing hydrocarbons in a large excess of hydrogen.

The extent of the decomposition of the alkyl halides caused by different relative concentrations of atomic hydrogen has also been investigated, as well as the variation in composition of the various products.

The methyl halides varied in reactivity toward atomic hydrogen under the conditions of our experiments from no reaction in the case of the fluoride to 100% reaction in the case of the iodide. About the same amount of ethyl bromide was decomposed as methyl bromide, but the decomposition of ethyl chloride was three-fold as great as methyl chloride.

The reaction of atomic hydrogen on the methyl halides produced methane, ethane, and possibly a trace of ethylene. The ethyl halides formed the same products but in different concentration.

The halogen of the alkyl halide appeared only as hydrogen halide in the case of the chlorides, but as free halogen and hydrogen halide in the experiments with the bromides and chlorides. The ratio of hydrogen halide to free halogen increased with an increase in atomic hydrogen concentration.

A possible mechanism to explain these results has been proposed and the heats of reaction for each of the possible primary reactions have been calculated.

The experimental results show that the heat of activation for the reaction of atomic hydrogen with the methyl halides must decrease rapidly from the fluoride to the iodide.

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(18) Grimm, *Handbuch Phys.*, **24**, 536 (1927).

All of the experimental results for the methyl halides can be explained by assuming that the primary reaction is $CH_3X + H = CH_3 + HX$.

The reactions with the ethyl halides were too complicated to warrant the proposal of a definite mechanism.

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Gaseous Thermal Diffusion—The Principal Cause of Discrepancies among Equilibrium Measurements on the Systems Fe_3O_4–H_2–Fe–H_2O, Fe_3O_4–H_2–FeO–H_2O and FeO–H_2–Fe–H_2O

BY P. H. EMMETT AND J. F. SHULTZ

When Sainte-Claire Deville[1] in 1870 first determined the ratio of water vapor to hydrogen in equilibrium with Fe–FeO, he pioneered the investigation of a system that up to the present has yielded puzzling and widely varying results. Although the apparatus devised by him and illustrated in principle in Fig. 1B has been used by practically all of the later workers, the experimental equilibrium water vapor–hydrogen ratios for a given temperature cover a considerable range of values, some being as much as 40% higher than others. Recently,[2] using a dynamic rather than a static type apparatus, we obtained experimental results for the equilibrium constants K_1 and K_2 of the reactions

$$FeO + H_2 = Fe + H_2O \qquad K_1 = H_2O/H_2 \qquad (1)$$

and

$$Fe_3O_4 + H_2 = 3FeO + H_2O \qquad K_2 = H_2O/H \qquad (2)$$

that were consistent among themselves and agreed with the values calculated indirectly from the Fe–C–O system[3] and the equilibrium constant[4] for the reaction

$$CO_2 + H_2 = CO + H_2O \qquad K_3 = (H_2O)(CO)/(CO_2)(H_2) \qquad (3)$$

Although there seemed to be little doubt that the flow experiments were correct, no entirely satisfactory explanation could be given for the 40% discrepancy between them and some of the carefully performed static experiments. Inasmuch as the source of error causing this gross uncertainty might be affecting the equilibrium constants not only for the Fe–H–O system but also for other equally important heterogeneous systems, a careful study was undertaken of the static types of apparatus and procedure used in previous experimental studies of the Fe–H–O system.

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(1) Sainte-Claire Deville, *Compt rend.*, 70, 1106, 1201 (1870); 71, 30 (1871).

(2) Emmett and Shultz, THIS JOURNAL, 52, 4268 (1930).

(3) E. D. Eastman, Bur. of Mines Circular 6125 (1929).

(4) Equation 38 from paper of Bryant, *Ind. Eng. Chem*, *23*, 1019 (1931).

The results of a part of this study have been presented briefly in a recent communication;[5] they seem to show that our previously reported values for K_1 and K_2 obtained by the use of a flow system are essentially correct and that the above-mentioned 40% discrepancy is to be attributed principally to an error caused by thermal diffusion in practically all previous static type experiments on equilibrium in the Fe–H–O system. In the course of the work it was found possible so to modify the usual static Deville type apparatus as to be able to perform static equilibrium experiments that consistently yielded correct values for K_1 and K_2 Accordingly, this apparatus was used in obtaining values of K_4 for the reaction.

$$^3/_4Fe_3O_4 + H_2 = {}^3/_4Fe + H_2O \qquad K_4 = H_2O/H_2$$

The primary purposes of the present paper are, therefore, to present the results of these static equilibrium experiments, to discuss in some detail the thermal diffusion measurements that have been made, and to show how the thermal diffusion factor operates in the usual static type apparatus.

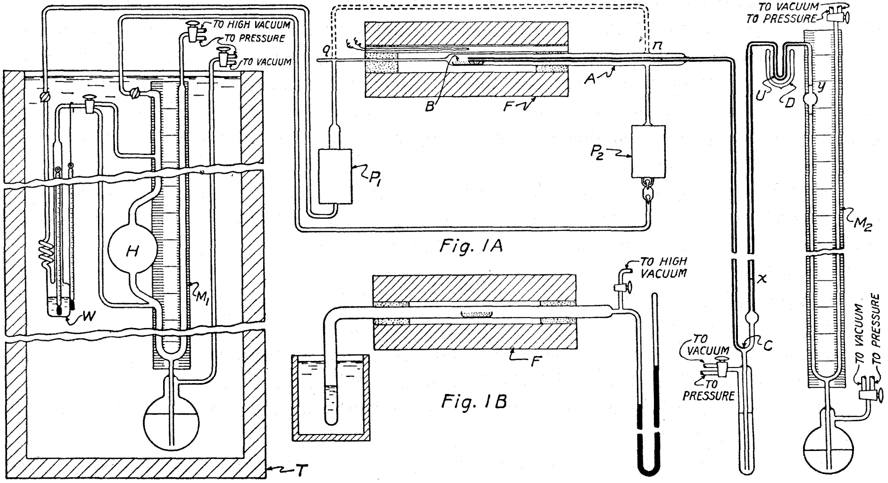

Fig. 1A

Fig. 1B

Fig. 1.

Equilibrium Constants for the Fe–H–O System

The final form of the static apparatus used in the present experiments and shown in Figure 1A was a modified Deville type. It consisted essentially of a 2-cm. quartz tube, **A,** containing a sample of the metal–metal oxide in boat B packed into a well insulated furnace F, and connected by quartz to Pyrex seals to Pyrex tubing leading to a water bulb **W,** and a 14-mm. mercury manometer M contained in the thermostat T. The latter was equipped with a glass front and was constructed according to specifications previously described.[6] P_1 and P_2 were all-glass circulating pumps by which the water vapor–hydrogen mixture in the reacting system could be circulated in either a clockwise or counter-clockwise direction[7] over the boat B, The actual rate of gas circulation

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(5) Emmett and Shultz, THIS JOURNAL, 54, 3780 (1982).

(6) Tremearne, *Ind. Eng Chem., Anal.* Ed , 2, 426 (1930).

(7) Porter, Lind and Bardwell, *Ind. Eng. Chem.*, 18, 1086 (1926).

effected by them in the present low pressure experiments was not accurately measured; at one atmosphere pressure, however, the pumps were capable of circulating 50 to 75 cc. of gas per minute against a pressure head of 2-3 mm. of water. The apparatus could be evacuated through the manometer M by a high vacuum pump. The exit pressure on the manometer was measured regularly by an attached McLeod gage not shown in the drawing. By the use of a telescope the pressure differences between the two arms of the manometer M were read on a carefully calibrated brass scale placed immediately behind the manometer arms. Bulb H of about 500 cc. capacity permitted the volume of the gas mixture being circulated over the solid phases to be changed to suit the particular experiment being carried out.

The first form of our static apparatus on which a majority of the experiments summarized below were carried out is not shown in the diagram but it differed from the final form in only a few minor details. Thus, the furnace was arranged vertically instead of horizontally, the oxide–metal charge being supported by a thin platinum gauze placed on the constriction between the 15-mm. quartz reaction tube and the 3-mm. quartz tubing projecting out of the lower end of the furnace. Furthermore, in the original apparatus the water bulb but not the mercury manometer was thermostated.

In the first apparatus we determined the temperature of the charge by two calibrated Pt–Rh thermocouples in conjunction with a type K Leeds and Northrup potentiometer. One of these was placed in a thin quartz shield in the center of the charge, the other directly opposite it but on the outside of the quartz reaction vessel. Since these experiments demonstrated the absence of an appreciable cross temperature gradient in the furnace, the inner thermocouple was omitted in the final set-up shown in Fig. 1A. Care was taken in this latter apparatus, however, to place the boat B directly opposite the thermocouple used.

Each tank of hydrogen used was analyzed for nitrogen. The amounts of gas consumed in an experiment were so regulated that the 0.1 to 0.2% nitrogen present in some of the tanks of hydrogen caused no measurable error in the final readings.

The oxide samples used were as follows.

Sample A was Fe_2O_3 No. 6, described in a previous paper.[8] It contained 0.12% of sodium hydroxide as impurity. It was reduced in *situ* to Fe_3O_4.

Sample B was a doubly promoted fused Fe_3O_4 used in preparing Fe synthetic ammonia catalysts.[9] It contained 0.35% Al_2O_3 and 0.08% K_2O.

Sample C was Fe_2O_3 No. 4, previously described[8] and contained 1.55% Al_2O_3 It was reduced *in situ* to Fe_3O_4.

Sample D was a pure Fe_2O_3 sample reduced to Fe_3O_4 at 400° by a 0.2:1 water vapor–hydrogen mixture.

Samples E and F were pure Fe_2O_3 samples reduced to Fe_3O_4 at 700° in a 1.8:1 water vapor–hydrogen mixture.

Sample G was pure Fe_2O_3 reduced at 700° by a 0.425:1 water vapor–hydrogen mixture.

The Fe_2O_3 used in samples B, E, F and G was prepared by drying ferric hydroxide precipitated from ferric nitrate solution by ammonium hydroxide.

The apparatus used in the reduction of samples D, E, F and G consisted of a 5-cm. quartz tube packed into a furnace and connected on the one end by a ground joint to a source of water vapor and hydrogen. Water vapor from a steam boiler, together with pure hydrogen from a flow meter, was passed through heated connecting tubes to two thermostated bead towers in series and then to the quartz reaction tube. The thermostat varied only ±0.1° during the preparation of a sample.

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(8) Emmett and Miss Love, J. *Phys. Chem.*, 34, 41 (1930).

(9) Larson and Richardson, Ind. *Eng. Chem.*, 17, 971 (1925).

In carrying out the static experiments, two or three preliminary oxidation or reduction runs were made when necessary to ensure the presence of both solid phases. Any possible surface effects that might result from an insufficient amount of one phase were thereby avoided

The results of the present static equilibrium experiments are shown in Tables I, II and IIX; they were obtained by circulating water vapor–

TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM Fe_3O_4–H_2–Fe–H_2O AS MEASURED IN A STATIC TYPE APPARATUS

Run	Sample	Temp., °C.	Initial H_2O/H_2	P_{total}, mm	P_{H_2O}, mm.	P_{H_2}, mm.	$K_4 = P_{H_2O}/P_{H_2}$	K_4 corrected to 400, 500 and 650, resp
43	A	401	0.111	136.4	13.38	123.0	0.108	0.107
92	B	408	.237	120.6	12.51	108.1	.115	.105
167	B	399	∞	128.0	13.05	115.0	.114	.115
168	B	401	.097	138.5	13.05	125.5	.104	.103
169	B	399	.212	129.2	13.05	116.2	.112	.113
202	C	401.5	.090	155.7	14.22	141.6	.100	.098
							Average for 400°	.107
44	A	502.5	.143	76.6	13.38	63.2	.211	.209
45	A	499	.161	77.4	13.47	63.9	.210	.210
47	A	502.5	∞	25.6	4.58	21.0	.218	.215
48	A	503.5	∞	24.8	4.58	20.2	.226	.222
96	B	501.5	∞	71.2	12.51	58.7	.213	.211
100	B	500.5	∞	74.6	13.17	61.4	.214	.214
101	B	502	.446	74.0	13.21	60.8	.217	.215
104b	B	500.5	.220	75.4	13.47	61.9	.217	.216
105	B	499.5	.207	76.0	13.47	62.5	.215	.215
170	B	502	∞	74.7	13.17	61.5	.214	.212
176	B	500.5	∞	75.2	13.25	62.0	.214	.213
179	B	500.5	.325	75.9	13.59	62.3	.218	.217
181	B	500	∞	75.9	13.68	62.2	.220	.220
182	B	502	.182	77.5	13.86	63.6	.218	.216
204	C	499.5	.133	83.7	14.26	69.4	.206	.207
256a	D	500	.255	100.0	17.50	82.5	.212	.212
258b	D	504	.229	97.2	17.50	79.7	.219	.214
							Average for 500°	.214
80	B	550	∞	54.8	12.19	42.6	.286	.286
81	B	549.5	∞	54.4	12.19	42.2	.289	.290
87	B	549.5	∞	54.8	12.23	42.6	.287	.288
88	B	550	∞	55.4	12.27	43.1	.284	.284
89	B	551.5	.210	55.8	12.27	43.5	.282	.280
172	B	551.5	∞	60.3	13.17	47.1	.279	.277
173	B	553	.350	59.5	13.21	46.3	.286	.282
174	B	550	.397	60.4	13.25	47.2	.281	.281
175	B	550	∞	60.5	13.25	47.3	.280	.280
178	B	550	∞	61.2	13.47	47.7	.282	.282
180	B	550.5	∞	62.1	13.68	48.4	.283	.282
205	C	550	.216	65.7	14.31	51.4	.279	.279
							Average for 550°	.283

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM Fe_3O_4–H_2–FeO–H_2O AS MEASURED IN A STATIC TYPE APPARATUS: SAMPLE E; P_{H_2O}, 17.50 MM.

Run	Temp., °C.	Initial H_2O/H_2	P_{total}, mm.	P_{H_2}, mm.	$K_4 = P_{H_2O}/P_{H_2}$,	K_4 corrected to 600, 700, 800°, resp.
279b	599	0.393	58.4	40.9	0.428	0.432
280	599	.660	55.0	37.5	.467	.471
281	598.5	.421	56.0	38.5	.454	.459
282	601	.507	54.2	36.7	.477	.473
283	599	.454	55.0	37.5	.467	.471
					Average for 600°	.461
268	701	.479	32.2	14.7	1.190	1.18
269a	699.5	.714	32.4	14.9	1.175	1.18
269b	700.0	1.224	32.4	14.9	1.175	1.18
270	699.5	0.854	32.6	15.1	1.158	1.16
271a	699.5	1.400	32.4	14.9	1.175	1.18
272	700.5	0.686	33.0	15.5	1.128	1.12
273	700.5	1.549	32.4	14.9	1.175	1.17
274	700.5	0.936	33.0	15.5	1.128	1.12
					Average for 700°	1.16
275	802.5	1.356	24.8	7.3	2.396	2.35
276	802.5	1.011	24.8	7.3	2.396	2.35
277	801.0	3.181	24.8	7.3	2.396	2.37
278	802.5	7.000	24.8	7.3	2.396	2.35
					Average for 800"	2.35

TABLE III

SUMMARY OF EQUILIBRIUM DATA FOR THE SYSTEM FeO–H_2–Fe–H_2O MEASURED IN A STATIC TYPE APPARATUS

	$K_1 = P_{H_2O}/P_{H_2}$			
Temp. °C.	By oxidation	By reduction	Average of static runs	By flow expts.[a]
600	0.334 (5)	0.334 (1)	0.334 (6)	0.332
700	.420 (27)	.418 (14)	.419 (41)	.422
800	.508 (6)	.496 (8)	.501 (14)	.499
900	.623 (4)	.576 (3)	.603 (7)	.594
1000	.682 (2)	.675 (3)	.678 (5)	.669

[a] See Emmett and Shultz, THIS JOURNAL, 52, 4268 (1930). Numbers in parentheses show number of runs averaged.

hydrogen mixtures in a counter-clockwise direction over an Fe–FeO, FeO–Fe_3O_4 or Fe–Fe_3O_4 sample through bulb W and back again to the reaction tube until over three successive fifteen-minute periods no pressure change occurred. Since comparatively few equilibrium data for the Fe-Fe_3O_4 system are available in the literature, Table I gives all of the completed experiments made on reaction 4. The only counter-clockwise runs omitted are those in which equilibrium was approached so slowly that a steady state could not be obtained during a single work day and those that were irregular because of temporary failure of the circulating pumps. A plot of the total pressure as a function of time yielded curves that left no uncertainty as to whether or not the circulating pumps had been functioning properly throughout a run. The table is practically self-explanatory. The pressures recorded in column 5 are the final ones read on manometer M, when a steady state had been reached. The vapor pressures of water are those given in the "International Critical Tables" for the observed temperatures which were read to 0.05° on a calibrated thermometer included in the reaction system and projecting into the water in bulb W. The hydrogen pressures of column 6 are the values of column 4 minus those of column 5. The average values of K_4 are 0.107, 0.214 and 0.283 at 400, 500 and 550°, respectively.

In Table II are shown all of the counter-clockwise experiments performed in the final static apparatus on the system Fe_3O_4–H_2–FeO–H_2O. These show constant reproducible H_2O/H_2 equilibrium ratios averaging 0.461, 1.16 and 2.35 at 600, 700 and 800°. They were obtained over sample E which was prepared by reducing Fe_2O_3 to Fe_3O_4 at 700° with a stream of 1.8:1 water vapor–hydrogen.

The runs on the Fe–FeO system were too numerous to be presented in detail. A summary of them is presented in Table III.

The averages of the values of K_2 and K_1 obtained in the present static experiments differ by less than 2% from those of our former flow experiment~.Thus, in the FeO–Fe_3O_4 system the flow and static results are, respectively, 1.18 and 1.16 at 700°, and 2.37 and 2.35 for 800°. The values for flow and static experiments in the Fe–FeO system are shown in columns 7 and 8, Table III.

The experimental errors involved in the static runs are small. Possible error in obtaining the absolute temperatures of the samples (±2°), in making each pressure reading (±0.2 mm.), and in reading the temperature of the water-bath (±0.05°), would mean maximum uncertainties of about ±0.004 in the individual values of K_4, ±0.003 for 600°, to 0.012 for 1000° in the values of K_1, and ±0.014, ±0.04 and ±0.13 in the values of K_2 at 600, 700 and 800°.

The experimental results presented in Tables I to III are for those runs in which counter-clockwise circulation was employed, the water vapor–hydrogen mixture passing quickly from the metal oxide sample through the small diameter quartz tube to water bulb W. It was invariably found, however, that if circulation in the opposite direction was employed so that the water vapor–hydrogen mixture passed from the metal–oxide sample along the large diameter quartz tube to the cool part of the apparatus, values of K_1, K_2 and K_4 were much higher than those shown and rather erratic. Thus at 700° the value of K_1 with clockwise circulation varied from 0.46 to 0.58. In fact many of the values obtained by clockwise circulating agreed well with those shown along curve 2, Fig. 2, being 30 to 40% higher than our own flow results or counter-clockwise static experiments. The results of these clockwise circulation experiments were at first baffling; however, they furnished a clue that led eventually to the phenomenon of thermal diffusion as the explanation not only of our own observations but of the many erroneously high values of K_1 and K_2 reported by various workers.

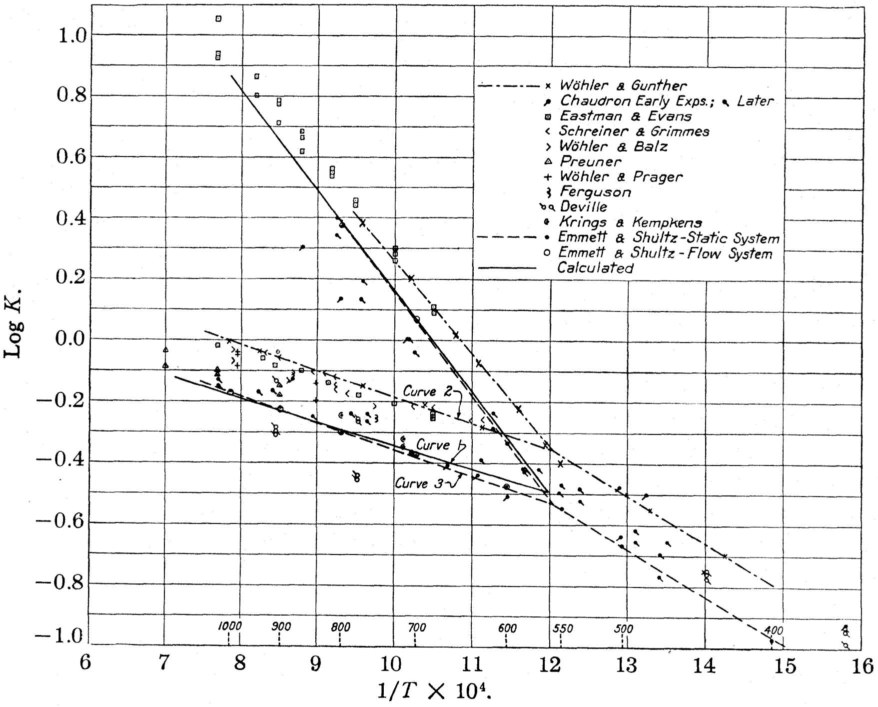

Fig. 2.

Thermal Diffusion as a Factor in Equilibrium Measurements on the Fe–H–O System.—According to the theory of thermal diffusion worked out by Chapman[10] and by Enskog[11] and verified for certain gas mixtures by a number of workers,[12] if two gases of different molecular weights such as water vapor and hydrogen are placed in a tube one end of which is heated while the other remains cold, the ratio of the heavy gas to the light gas rapidly becomes and remains larger in the cold end of the tube than in the hot end. It seemed probable that in accordance with this theory the water vapor–hydrogen ratio in the "cold end" of a Deville type apparatus would be higher than in the "hot end." Furthermore, calculations made by equations developed by Chapman showed that assuming the molecules of

(10) Chapman, *Proc. Roy. Soc.* (London), *93*, 1 (1916); *Phil. Trans. Roy. Soc.*, *217*, 115 (1917); *Phil. Mag.*, *48*, *602* (1924).

(11) D. Enskog, *Physik. Z.*, *12*, *538* (1911); *Ann. Physik*, 38, 742 (1912).

(12) For a complete bibliography on thermal diffusion see Ibbs and Grew, *Proc. Phys. Soc.*, *43*, 142 (1931).

water vapor and of hydrogen to be elastic spherical shells of diameters[13] 2.29 and 1.36 Å., respectively, the possible thermal separation that could occur is about twice as great as the largest observed discrepancies.

In order to prove that this thermal diffusion factor actually does account for the large observed discrepancies in Fe–H–O equilibrium data the apparatus shown in Fig. 1A was so modified as to permit an actual determination of the water vapor–hydrogen ratios to be made simultaneously in the hot and cold ends of tube A. The Pyrex tube between pump P and furnace F was sealed off at q; then a connecting line from q to n was inserted as shown by the dotted line in Fig. 1A. This permitted the water vapor–hydrogen mixture to be circulated across the cold end of A. By diffusion this gas mixture could penetrate the hot portion of tube A and reach the metal–oxide sample. Finally a 1-mm. quartz capillary tube was fastened by a quartz–Pyrex seal to a 0.2-mm. capillary tube and sealed into tube A as shown in Fig. 1A. This capillary was then connected through a mercury cut-off C to a gas buret and another manometer M_2 as shown.

By lowering the mercury in C a sample of water vapor–hydrogen from the "hot end" of the quartz reaction tube could be collected in the buret between the marks x and y, at a pressure p_1. By circulating the gas sample back and forth through the capillary U surrounded by liquid air in the Dewar flask D the water vapor could be frozen out, leaving hydrogen at pressure p_2'. The water vapor–hydrogen ratio is equal to $(p_1 - p_2)/p_2$, where p_2 is the value of the hydrogen pressure, corrected for the slight pressure change caused by cooling the gas in "U." The volume of the capillary immersed in liquid air was ordinarily only a few hundredths of a cc. out of a total buret volume of about 4 cc., so the correction to p_2' was small. In making an actual analysis it was customary first to remove and pump out the small amount of gas from the sampling capillary down to the gas buret about five minutes before the regular analysis was taken. This increased somewhat the accuracy of the analytical determinations by making the gas sample taken for analysis more nearly the composition of the gas mixture actually present at the moment of sampling in the hot part of the reaction tube.

A comparison of the composition of the water vapor–hydrogen mixture in the hot and the cold ends of the reaction tube is shown in Table IV. Columns 3 and 4 give the water vapor–hydrogen ratios calculated by reading the total pressure in A on manometer C and noting the temperature of the water in bulb W; the analytical results are shown in columns 5, 6 and 7. Although the observational errors were necessarily rather large, this method of analysis proved quite satisfactory. Assuming an accuracy of ±0.2 mm. in each pressure reading on the manometer M_2 used in the analytical determinations, there might be a maximum error in any one

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[13] Jeans, "Dynamic Theory of Gases," p. 327.

water vapor–hydrogen analysis from 3 to 5%, depending upon the partial pressures of hydrogen and water vapor in the sample chosen.

TABLE IV

THERMAL DIFFUSION EXPERIMENTS USING Fe–FeO OR Fe_3O_4–FeO SAMPLES

Run	Temp., °C.	By manometer Initial H_2O/H_2	 Final H_2O/H_2	Initial pressure $P_{H_2O} + P_{H_2}$, mm.	By analysis Final pressure P_{H_2} (corrected), mm.	P_{H_2O}/P_{H_2}
		Fe–FeO System (Sample F)				
284a	700	0.207	0.548	46.0	32.7	0.40
284b	702.5	.559	.548	53.8	38.0	.42
286a	700	.353	.623	97.0	71.2	.36
286b	699	.660	.646	54.4	37.4	.45
288a	800	.269	.708	48.6	32.7	.49
289	801	.744	.708	48.0	32.7	.47
290a	900	.299	.821	49.8	31.5	.58
290b	902	.854	.821	43.0	28.0	.54
290c	899	.854	.821	45.6	29.6	.54
291a	1001	.304	.966	46.0	26.8	.72
291b	1001	1.011	.966	46.2	27.9	.65
291c	1001	1.035	.966	44.0	26.9	.64
		FeO–Fe_3O_4 System (Sample G)				
297a	700	0.193	1.495	27.4	12.1	1.26
297b	700.5	1.521	1.495	26.4	12.1	1.18
297c	699.5	1.521	1.495	35.6	16.5	1.15
298a	800	0.402	3.181	31.6	9.5	2.33
298b	800.5	3.301	3.181	31.6	9.4	2.36
298c	800	3.430	3.181	32.0	9.6	2.33
298d	800	3.430	3.181	30.4	9.0	2.38

TABLE V

SUMMARY OF THERMAL DIFFUSION RESULTS ON Fe–H–O SYSTEM

System	Temp., °C.	Water–hydrogen ratio In "cold end" by manometer	 Best values[a] of previous static expts.	 In "hot end" by analysis	 In flow experiments[b]
Fe–FeO	700	0.57	0.584	0.41	0.422
Fe–FeO	800	.71	.706	.48	.499
Fe–FeO	900	.82	.822	.55	.594
Fe–FeO	1000	.97	.937	.67	.669
FeO–Fe_3O_4	700	1.50	1.45	1.20	1.181
FeO–Fe_3O_4	800	3.18	2.98	2.35	2.372

[a] See Eastman and Evans, THIS JOURNAL, 46, 888 (1924). [b] See Emmett and Shultz, *ibid.*, 52, 4268 (1930).

The summary of various experimental results given in Table V can in our opinion leave no reasonable doubt that owing to the action of thermal diffusion the "best values" for K_1 and K_2 obtained by previous static experiments are about 40% high and that our own flow and static experiments are essentially correct. The water vapor–hydrogen ratios given in

TABLE VI

THERMAL SEPARATION OF WATER VAPOR–HYDROGEN MIXTURES AT 400–500°

Temp., °C.	"Cold end" H_2O/H_2	"Hot end" H_2O/H_2	Percentage water vapor In "cold end"	In "hot end"	Difference
499	0.275	0.180	21.6	15.3	6.3
506	.284	.201	22.1	16.7	5.4
502	.285	.215	22.2	17.7	4.5
405	.297	.225	23.0	18.4	4.6
404	.297	.215	23.0	17.7	5.3

column 3 were obtained by an apparatus and procedure identical in all important respects to that used by Eastman and Evans,[14] Schreiner and Grimmes,[15] Wohler and Günther[16] and van Groningen,[17] in that a water vapor–hydrogen mixture was permitted to diffuse from the cold end of a large diameter tube to the "hot end" of the same tube and there equilibrate with an Fe–FeO or Fe_3O_4–FeO sample. As in their experiments, the water vapor–hydrogen ratio was taken as the ratio of the P_{H_2O} in the thermostated water bulb W to the difference between the total pressure in **the** apparatus and the P_{H_2O}. These readings of column **3** agree excellently with the "best values" of the above-mentioned previous static experiments given in column 4 and yet are 40% too high. The composition of the water vapor–hydrogen mixture actually present in the hot end of the reaction tube is given in column 5 by the analysis of samples taken directly from the hot end of the apparatus. Our confidence in the essential correctness of the values of K_1 and K_2 obtained by our static and flow experiments rests upon their agreement with each other, with the results of the direct analysis of column 5, Table V, and with the values calculated from the Fe–C–O system with the help of K_3.

The diffusion data also make clear why our static experiments performed in the apparatus shown in Fig. 1A were correct only when the water vapor–hydrogen mixture was circulated in a counter-clockwise direction. When a steady state is attained in a given experiment at say 700° the gas composition in the "hot end" of the reaction tube will be about 0.41 to 0.42, as shown in column 5, regardless of the direction of circulation. Furthermore, the "cold end" water vapor–hydrogen ratio will be much higher, approaching 0.57 or 0.58, if the gas mixing caused by the pump circulation is not too great. It now becomes evident that circulating the gaseous mixture in a counter-clockwise direction to a steady state and taking the usual manometer and temperature readings is in reality merely a means of analyzing the "hot end" H_2O–H_2 mixture, for the linear velocity of the gas passing along the 3-mm. quartz tube toward q is sufficiently high

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(14) Eastman and Evans, THIS JOURNAL, 46, 888 (1924)

(15) Schreiner and Grimmes, Z. *anorg. allgem. Chem.*, *110*, 311 (1920).

(16) Wohler and Gunther, *Z. Elektrochem.*, 29, 276 (1923).

(17) Van Groningen, Dissertation, Delft, 1921. Our conclusions relative to Van Groningen's results are based on statements of Wohler and Gunther as the original dissertation was not available to us.

to prevent a change in composition of the gas mixture by thermal diffusion at the 700° to room temperature transition point. The observed water vapor–hydrogen ratio, therefore, will be the one existing in the hot end of **A** in equilibrium with the Fe–FeO sample. Clockwise circulation to a steady state, on the other hand, merely analyzes the "cold end" steam–hydrogen mixture giving an observed K_1 value of about 0.57 or 0.58, which is approximately 40% higher than that existing in the "hot end" of the apparatus. It thus becomes clear why our own clockwise results gave high water vapor–hydrogen ratios whereas our counter-clockwise experiments gave correct values of K_1, K_2 and K_4.

It may be well to point out that if clockwise rather than counter-clockwise gas circulation is employed, our apparatus becomes essentially the same as that used by Wöhler and Balz,[18] Wohler and Präeger[19] and Chaudron,[20] in that a slow circulation of gas from the "hot end" to the "cold end" of a large diameter reaction tube occurs. In agreement with our own clockwise experiments, they obtained erratic values that were from 5 to 40% too high. It seems probable that thermal diffusion also caused the principal errors in their work.

Although the diffusion experiments of Tables IV and V seem to substantiate and prove the correctness of our data on the Fe–FeO and FeO–Fe_3O_4 systems it remained to prove that at 400 and 500° thermal diffusion could account for the rather large differences between our own results on the Fe–Fe_3O_4 system shown on curve 3, Fig. 2, and those of Wohler and Giinther shown on curve 2. However, diffusion experiments on the Fe–Fe_3O_4 system similar to those obtained above for the FeO–Fe and FeO–Fe_3O_4 systems proved impractical because of the slowness with which equilibrium was attained at temperatures of 400 to 500° in the Fe–Fe_3O_4 system. Accordingly, diffusion experiments were performed without a metal–oxide sample in the quartz reaction tube. The apparatus was connected as in our previous diffusion experiments. Sufficient hydrogen was admitted to form "cold end" water vapor–hydrogen ratios shown in column 2, Table VI. After about thirty to sixty minutes circulation of the gas mixture across tube **A** by the circulating pumps, the analytical values shown in column **3** were obtained.

The differences between the water vapor–hydrogen ratios in columns 2 and 3, Table VI, can be seen to be qualitatively the same as the difference between the 0.107 value for curve **3** and the 0.162 value for curve 2, at 400°; or the 0.214 value for curve **3** and the 0.320 for curve 2, at 500°.

The number of thermal diffusion experiments at 400 and 500° is, however, too small to warrant rigorous quantitative comparisons. Neverthe-

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(18) **Wbhler and Balz, Z.** ***Elektrochem*** **, 27, 406 (1921).**

(19) Wohler **and Praeger,** ***ibid.*****, 23, 199 (1917).**

(20) **Chaudron, Ann.** ***chim. phys.*****, 16, 221 (1921).**

less, it may be of interest to point out that the largest observed differences between the cold end water vapor–hydrogen ratios in column 2 and the hot end ratios in column **3** do account quantitatively for the discrepancy between curves 2 and **3** at 400 and 500°. It seems fair to conclude, therefore, that our own values of K_4 shown in Table III are essentially correct whereas those of previous workers are as much as 50% too high because of the thermal diffusion factor.

Discussion

The results of various experimental determinations of K_1, K_2 and K_4 have been plotted in Fig. 2. Of the static experiments, all but the early ones of Deville,' Chaudron[21] and Preuner[22] have been discussed and seem to be in error because of thermal diffusion. The experiments of these workers have been considered fully in previous publications;[5,14] various sources of error other than thermal diffusion have already been attributed to them. Consequently, their work need not be discussed here in detail; it will suffice to point out that the experimental results both of Chaudron and Deville probably should have been high because of thermal diffusion, whereas those of Preuner should not have been far in error. As can be seen from Fig. 2, Preuner's results are from about **3** to 16% high; those of Deville, when corrected for various probable sources of error, are 15 to 25% high; and those of Chaudron are from 0 to 40% high. The two or three approximately correct values of K_1 obtained by Chaudron in the 600 to 700° region seem to be either the result of certain errors compensating for the thermal diffusion factor, or of some unexplained detail of procedure stirring the water vapor–hydrogen mixture effectively and eliminating the thermal diffusion error. His results are certainly not sufficiently consistent to be considered valid exceptions to our general conclusions relative to thermal diffusion.

Although our static and flow experiments agree in general with curve 1 obtained indirectly by combining values of K_3 and values for equilibrium constants in the Fe–C–O system, it will be noticed that at 600 and 700° in particular our results seem to be a few per cent. lower and at 900 and 1000° a per cent. or so higher than curve 1. We were at first inclined to attribute this to a combination of possible experimental errors in our own results, and uncertainties in the values of K_3 used in calculating curve 1. Completion of the Fe–Fe_3O_4 experiments, however, has furnished one definite bit of evidence that curve **3** probably represents the value of K_1 and K_2 more accurately than curve 1. Eastman has pointed out that K_4 must be equal to $K_1^{1/4} \cdot K_2^{3/4}$ where K_1 and K_2 are obtained by extrapolation of the equilibrium curves from above the triple point Fe–FeO–Fe_3O_4 down to 400 or 500°. Such extrapolations and calculations

[21] *Chaudron, Compt.* rend., **159**, 237 (1914).

[22] *Preuner, Z. physik. Chem., 47,* 385 (1904).

from curve 1 lead to K_4 values of 0.238 and 0.127 at 500 and 400°, respectively, instead of our experimental values of 0.214 and 0.107. On the other hand, analogous calculations of K_4 from curve 3 yield values in satisfactory agreement with our own experimental results. We are, therefore, inclined to believe that curve 3 represents the Fe–H–O equilibria even more accurately than curve 1 and that the difference between these two curves is due either to slight errors in the present "best values" of the equilibrium constants for the Fe–C–O system or in the values of K_3 or in both.

The question naturally arises as to whether the thermal diffusion factor may not also have influenced the measurements of the CO_2/CO ratios reported for the equilibrium in the Fe–C–O system. calculations based on the thermal diffusion measurements of Ibbs and Underwood[23] on carbon monoxide–carban dioxide mixtures do indeed indicate the possibility of considerable errors in the Fe–C–O equilibrium data. Thus if equilibrium with respect to thermal diffusion were established the "cold end" CO_2/CO ratios for the Fe–FeO system might be higher than the "hot end" values by as much as 6.3% at 600° to 7.9% at 1000°. The actual errors in published CO_2/CO data that can be attributed to thermal separation are, however, uncertain for two reasons. In the first place, frequently authors do not state whether the carbon dioxide–carbon monoxide mixture taken for analysis is from the "hot end or "cold end" of the apparatus. Second, almost all studies of the Fe–CO_2–FeO–CO system have been made at nearly one atmosphere pressure where diffusion is slower and convection currents are likely to cut down considerably the amount of thermal separation occurring between the hot and cold ends of the usual reaction vessel. Only some careful experiments on the Fe–C–O system made in such a way as to avoid any thermal separation of the carbon monoxide–carbon dioxide mixtures can definitely prove whether or not the "best values" for the Fe–C–O system reported by Eastman[3] are free of any thermal diffusion errors.

The apparatus used in the present studies was not well adapted to the determination of the actual and accurate composition of the phases that we have freely spoken of as Fe, FeO and Fe_3O_4. Although the initial composition of the sample and the total amount of oxygen added or removed were always known, it was impossible to say whether the steady state obtained during the one to six hours run employed in the present studies corresponded to equilibrium with the sample as a whole or with only the outer few layers of molecules in the individual solid particles. Experiments extending over much longer equilibration periods would be needed to establish definitely the variation of the water vapor–hydrogen equilibrium ratio with the composition of any solid solutions that might

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(23) Ibbs and Underwood, *Proc. Phys. Soc.*, 39, 227 (1927).

exist in the iron–oxygen system. The results of Krings and Kempkens,[24] however, make it seem very probable that our Fe phase contained at the most a few tenths of one per cent: of oxygen. The FeO in the present experiments is probably the low oxygen limit of any $FeO–O_2$ solid solution that may exist.[25] On the other hand, the Fe_3O_4 employed in the $FeO–Fe_3O_4$ equilibrium experiments was probably the upper limit of any solid solution existing between Fe_3O_4 and small amounts of FeO as it was prepared by passing a 1.8:1 water vapor–hydrogen mixture over Fe_2O_3 at 700°.

The temperature at which the three solid phases, Fe, FeO and Fe_3O_4 can be in equilibrium with a water vapor–hydrogen mixture is about 559° according to the experimental values for K_1, K_2 and K_3, shown along curve **3.** This seems definitely lower than the 570° value usually assumed for this point.

In previous publications[5] a tentative explanation for the various discrepancies in Fe–H–O equilibrium studies was made by assuming that a "surface effect" may have been present as a disturbing factor. Our present static experiments, however, have shown that such surface effects cannot account for the consistently high values frequently reported for K_1 and K_2; they may, however, have been factors in the erratic behavior of certain previous experiments, particularly those of Preuner.[22]

No data have appeared in the literature so far relative to the separation of water vapor–hydrogen mixtures that may result for different temperature gradients in consequence of thermal diffusion. The data reported in Tables IV to VI above can in no sense be considered to represent necessarily the maximum thermal separation that may occur in water vapor–hydrogen mixtures as a result of the temperature gradients here existing. It is safe to conclude, however, that within the experimental errors of the present work, they can be considered minimum values for such thermal separation.

Summary

A modified Deville type static apparatus is described by which the equilibrium ratios of water vapor–hydrogen have been found to be 0.334, 0.419, 0.501, 0.603 and 0.678 at 600, 700, 800, 900 and 1000" for the Fe–FeO system; 0.107, 0.214 and 0.283 at 400, 500 and 550" for the $Fe–Fe_3O_4$ system; and 2.35, 1.16 and 0.461 at 800, 700 and 600° for the $FeO–Fe_3O_4$ system. Thermal diffusion has been shown to account for previous static values being as much as 40% too high. The change in composition of water vapor–hydrogen mixtures because of thermal diffusion has been measured in the absence of an oxide sample at 400 and 500°. The possible influence of the thermal diffusion factor on the system Fe–C–O has been discussed.

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[24] Krings and Kempkens, *Z. anorg. allgem. Chem.*, *183*, 225 (1924); 190, 313 (1930).

[25] Ralston, Bull. 290, U. S. Bureau of Mines (1929).

{CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

Equilibrium in the System SnO_2–H_2–Sn–H_2O. Indirect Calculation of the Values of the Water Gas Equilibrium Constants

BY P. H. EMMETT AND J. F. SHULTZ

In previous publications[1] we have shown that thermal diffusion by creating a difference between the composition of a water vapor–hydrogen mixture in the hot end and that in the cold end of a reaction tube has been responsible for many of the experimental values for the equilibrium constants in the Fe–H–O system being as much as 40% too high. It seemed very probable that the same phenomenon had caused the values of K_1 obtained by Eastman and Robinson[2] for the reaction

$$\frac{1}{2}SnO_2 + H_2 = \frac{1}{2}Sn + H_2O \qquad K_1 = H_2O/H_2$$

to be similarly in error. We have, accordingly, redetermined the value of K_1 using the apparatus and procedure that has previously been shown to eliminate thermal diffusion errors in determining values of the equilibrium constants for the Fe–H–O system.[3] The sample of SnO_2 used was prepared by dissolving C. P. tin in nitric acid, heating the resulting stannic acid to expel the moisture and finally igniting it in air to 500 or 600°. The 3-g. SnO_2 sample was partially reduced in *situ* before the final experiments.

Results

The experimental results are shown in Table I. The total pressures (column 4) were read on a mercury manometer. The partial pressure of water vapor as obtained from the "International Critical Tables" for the

TABLE I

EQUILIBRIUM MEASUREMENTS ON THE SYSTEM SnO_2–H_2–Sn–H_2O

Run	Temp., °C.	Initial H_2O/H_2	p_{total}, mm.	$K_1 = p_{H_2O}/p_{H_2}$	K_1 corr. to 600, 700, 750 and 800°C., resp.
26	650.5	0.837	38.4	1.61	1.61
27	650.0	5.51	37.2	1.76	1.76
38	650.0	0.757	38.4	1.61	1.61
29	651.0	2.097	37.8	1.68	1.67
				Average for 650°	1.66
17	700.5	0.837	34.4	2.21	2.20
18	701.5	0.952	34.2	2.25	2.23
19	700.5	∞	34.2	2.25	2.24
20	700.0	0.603	34.6	2.17	2.17
21	700.5	∞	34.2	2.25	2.24
				Average for 700°	2.22

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(1) Emmett and Shultz, THIS JOURNAL, 54, 3780 (1932).

(2) Eastman and Robinson. *ibid.*, 50, 1106 (1928).

(3) The apparatus is that shown in Fig. 1A of a preceding article on the Fe–H–O system by Emmett and Shultz, THIS JOURNAL, 55, 1376 (1933); the procedure was identical with that there described.

TABLE I (Concluded)

Run	Temp., °C.	Initial H_2O/H_2	P_{total} mm.	$K_1 = P_{H_2O}/P_{H_2}$	K_1 corr to 600, 700, 750 and 800 °C., resp.
22	751.0	0.578	32.0	2.85	2.84
23	749.5	0.619	32.0	2.85	2 86
24	750.5	m	32.2	2.79	2.78
25	749.5	m	32.0	2.85	2.86
				Average for 750°	2.84
12	799.5	7.18	30 4	3.54	3 55
13	800.0	0.653	3n 6	3 44	**3 44**
14	799.5	0.734	30 4	3 54	3.55
15	800.0	∞	30 4	3 54	3.54
16	799.5	∞	30.4	3.54	3.55
				Average for 800°	3.53

temperatures of the thermostated water bulb included in the reaction system was 23.7 mm. in all runs. The hydrogen pressures used in calculating K_1 are the differences between the total pressures in the system and the partial pressures of water vapor.

If the temperature of the metal oxide sample is considered accurate to ±2°, that of the water-bath to ±0.05°, and the pressure readings to ±0.2 mm., the total uncertainty that might exist as to the value of K_1 given by any one experiment would be ±0.06 unit at 650° C., ±0.09 at 700, ±0.13 at 750 and ±0.18 at 800°. The probable errors calculated from the runs shown in Table I are of course very much smaller.

Our experimental results are summarized in Table II. The values obtained by static and by dynamic experiments of Eastman and Robinson[2] are included for comparison, as also are the values of K_1 calculated from the values of K_2 for the reaction

$$^1/_2SnO_2 + CO = {}^1/_2Sn + CO_2 \qquad K_2 = CO_2/CO$$

together with the value of the constant K_3 [4] for the reaction

$$H_2 + CO_2 = CO + H_2O \qquad K_3 = \frac{(CO)\,(H_2O)}{(CO_2)\,(H_2)}$$

In Fig. 1 are plotted our data (curve 2) as well as those of Eastman and Robinson obtained by static experiments (curve 3) and by dynamic experiments (curve 4). Curve 1 shows the equilibrium water vapor–hydrogen ratio calculated indirectly with the assistance of the Sn–C–O data of Eastman and Robinson and values of the water gas constant K_3.

Discussion **and** Conclusion

As can be seen in Fig. 1, curves 1 and 2 agree approximately with each other, but represent values of K_1 about 25% lower than those obtained in the static experiments of Eastman and Robinson (curve 3). Furthermore, the difference in composition between the water vapor–hydrogen

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(4) The values of K_3 used were obtained from equation 38 given by Bryant, *Ind. Eng.* Chem., 23, 1019 (1931).

mixture corresponding to curve *2* and those corresponding to curve **3** is in approximate agreement with that obtained for comparable water vapor–hydrogen ratios and temperature gradients in the Fe–H–O equilibrium studies. Probably, then, their values of K_1 really show the steady state composition of the water vapor–hydrogen mixture in the cold end of the static apparatus rather than the equilibrium ratio existing in the hot end of the apparatus in contact with $Sn-SnO_2$. Thus, values of K_1 obtained in the static experiments of Eastman and Robinson and shown by curve **3** seem to be about 30% high because of the same thermal diffusion factor responsible for errors in similar studies on the Fe–H–O system.

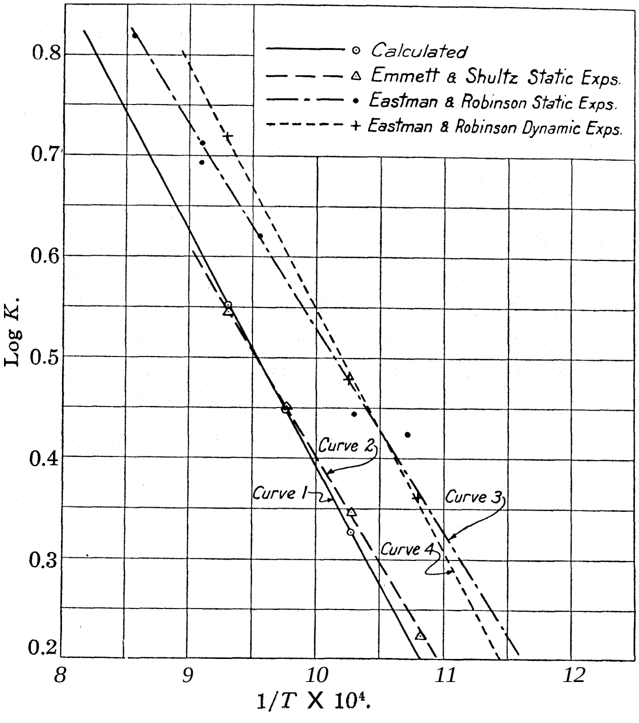

Fig. 1.—Variation with $1/T$ of $\log K$, where $K = H_2O/H_2$ in equilibrium with $Sn-SnO_2$. The calculated values of K represented by curve 1 were obtained by combining the equilibrium data of Eastman and Robinson for the Sn–C–O system with values for the water gas constant K_3 given by free energy equation **38** in the paper of Bryant.[4]

It seems odd, at first, that a dynamic system such as used in obtaining curve 4 could be in error due to thermal diffusion. However, a dynamic or flow system can involve errors due to thermal diffusion as readily as a static system provided the rate of gas passage through the reaction vessel is sufficiently low. In the paper of Eastman and Robinson the rate of gas passage was not given; it might have been small enough to have permitted the water vapor–hydrogen mixture in the cold end of the large diameter inlet tube to have become much larger than that in the hot reaction bulb. At any rate, the 655 and 703° points but not the 809° point in their dynamic experiments can be accounted for by the same amount of thermal diffusion that explains the difference between the curves 2 and 3; the reason for the 809° point being considerably above curve **3** is not clear.

From the summary given in Table II the values of K_1 calculated indirectly from the Sn–C–O equilibrium data and the water gas constant K_3 can be seen to agree approximately with our own directly measured values. The agreement is probably within the combined experimental error of our own experiments and those on the Sn–C–O system. The indirectly calculated values of K_1 in column **A** are based upon the Sn–C–O data of Eastman and Robinson; those in column B on the data of Meyers and Scheffer.[5]

TABLE II

SUMMARY OF EQUILIBRIUM DATA ON THE SN–H–O SYSTEM. VALUES OF $K_1 = H_2O/H_2$

Temp., °C.	Present expts.	Static expts. Eastman and Robinson	Dynamic expts. Eastman and Robinson	Calcd.[a] from water gas constant and Sn–C–O data A	B	C
650	1.66	2.30	2.26	1.59	1.73	1.64
700	2.22	2.97	3.02	2.12	2.30	2.17
750	2.84	3.76	..	2.81	2.95	2.79
800	3.53	4.66	5.19	3.57	3.70	3.50

[a] Column **A** is based on the Sn–C–O data of Eastman and Robinson; columns B and C on those of Meyers and Scheffer. The Sn–C–O data used in calculating column C have been corrected for possible thermal diffusion errors by the thermal diffusion data of Ibbs and Underwood[6] on carbon monoxide–carbon dioxide mixtures.

It is interesting to note that the indirectly calculated values of K_1 (column C) based upon K_2 values of Meyers and Scheffer that have been corrected for possible thermal diffusion errors[6] agree quite well with our own data. Whether any thermal diffusion errors actually did enter into the Sn–C–O experiments of either Eastman and Robinson or Meyers and Scheffer can of course only be decided by some careful experiments so carried out as to prevent the composition of the CO_2–CO mixture in the hot part of the reaction vessel being different from that in the cold part.

The equilibrium data reported in the present paper remove the last large discrepancy between the directly measured values for the water gas equilibrium constant, K_3, and those calculated indirectly by combining the equilibrium data for various metal–oxide–CO–CO_2 and metal–oxide–

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(5) Maeda [Bull *Inst. Phys. Chem. Research* (Tokyo). *2,* 330 (1923)] and Fraenkel and Snipischski [*Z. anorg. allgem. Chem.,* **125,** 235 (1922)] have also obtained experimental equilibrium values for the system Sn–C–O. Their work which has been criticized both by Eastman and Robinson and by Meyers and Scheffer has not been used in any calculations in the present paper.

(6) The experimental data of Ibbs and Underwood [Proc. *Phys Soc.*, 39,227 (1927)] on thermal diffusion in carbon monoxide–carbon dioxide mixtures make it possible to calculate the maximum error in the values of K_2 that might have been caused by thermal diffusion in the experiments of Meyers and Scheffer.

H_2O–H_2 systems. In Table III, accordingly, have been summarized the various indirectly calculated and the directly measured values for the water gas equilibrium constants between 400 and 1000°. For comparison the values of the constants obtained from free energy equations **38** and **39** of a recent paper by Bryant[4] have been included. Bryant's equations were formulated from thermal data of various authors for CO, CO_2, H_2O and H_2, together with the 986° directly measured equilibrium value from the work of Neumann and Köhler.[7]

TABLE III

VALUES OF THE WATER GAS EQUILIBRIUM CONSTANT, $K_2 = (CO)(H_2O)/(CO_2)(H_2)$

Temp. °C.	Direct measurements		Calculated from equations of Bryant		Calculated[a] from H_2O–H_2 and CO_2–CO equilibria with				
	Hahn	Neumann and Köhler	Equation 38	Equation 39	Co–CoO	Fe–FeO	FeO–Fe_3O_4	Sn–SnO_2 A	Sn–SnO_2 B
350		0.041							
400		.080	0.087	0.082					
450		.140	.139	.132	0.137				
500		.200	.205	.197	.207				
550		.290	.292	.281	.297				
600		.410	.394	.378		0.383	0.384		
650		.50	.507	.491		(.488)	(.494)	0.533	0.486
700	0.610	.63	.638	.624		.622	.630	.657	.617
750	.755	.78	.782	.771		(.770)	(.776)	.787	.751
800	.906	.93	.938	.933		.919	.918	.918	.893
850	1.071	1.09	1.11	1.10		(1.11)			
900	1.240	1.29	1.29	1.28		1.315			
950	1.420	1.44	1.48	1.48		(1.50)			
1000	1.606	1.66	1.67	1.68		1.699			

[a] The water vapor–hydrogen ratios and carbon dioxide-carbon monoxide ratios for the Co–CoO calculation, as well as the water vapor–hydrogen ratios for the Fe–FeO, FeO–Fe_3O_4 and Sn–SnO_2 calculations, were taken from our equilibrium studies. The CO–CO_2 equilibrium data for the Fe–FeO and FeO–Fe_3O_4 systems are the "best value" given by Eastman in Circular **6125,** U. S. Bur. of Mines (1929). The CO–CO_2 equilibrium data for the Sn–SnO_2 system were obtained from the paper of Eastman and Robinson (A) and the paper of Meyers and Scheffer (B). The values inclosed in parentheses involve interpolations in the data on the Fe–H–O system.

The agreement as a whole is very satisfactory; certainly no large errors in the values of the water gas constants between 400 and 1000° now exist. The direct measurements of Hahn[8] are from 2 to 4% lower than the values of K_2 given by equation **39.** Those of Neumann and Kohler agree in general decidedly better with equation **38** than with equation **39,** as do also the indirect calculations based on equilibria with the Co–CoO system.[9] In the temperature range 600 to 800°, however, indirect calculations based on the Fe–FeO and FeO–Fe_3O_4 systems agree very well with equation **39** but are 2 to 3% lower than the values given by equation **38.** It may be

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(7) Neumann and Kohler. Z. *Elektrochem.*, **34**, 227 (1928).

(8) Hahn, *Z. physik. Chem.*. **42**, 705 (1903); **44**, 513 (1903); **46**, 735 (1903)

(9) Emmett and Shultz, THIS JOURNAL, **51**, 3249 (1929); **52**, 892 (1930).

noted in this connection that any errors caused by thermal separation in the carbon dioxide–carbon monoxide mixtures in Fe–C–O equilibrium measurements[10] would cause the values of K_3 calculated from the Fe–C–O and the Fe–H–O data to be low; accordingly the 2 or 3% difference between equation 38 and the values of K_2 thus indirectly calculated might easily be due to such errors in the Fe–C–O data. The direct calculations of K_3 based on our own data for the Sn–H–O system and those both of Eastman and Robinson (A) and Meyers and Scheffer (B) for the Sn–C–O system have been included since it is not possible at present to decide which of the two sets of experimental values of K_2 is the more reliable. It should be noted, however, that as pointed out above the *3* or 4% discrepancy between the values of K_3 in column B and those of equation 38 could be due entirely to thermal diffusion errors in the experiments of Meyers and Scheffer on the Sn–C–0 system.

Summary

Values of the equilibrium constant H_2O/H_2 for the reaction $^1/_2\ SnO_2 + H_2 = {}^1/_2\ Sn + H_2O$ have been found to be 1.66, 2.22, 2.84, and 3.53 at 650, 700, 750 and 800°. These values are about 25% lower than the results of previous workers, and when combined with equilibrium data for the Sn–C–O system give values for the water gas constant that agree within a few per cent. with those obtained by direct measurements.

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[10] See Eastman and Evans, THIS JOURNAL, 46, 888 (1924).

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[CONTRIBUTION NO. 260 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Recombination of Hydrogen Atoms. I

BY I. AMDUR[1] WITH A. L. ROBINSON

Introduction

The rate of recombination of hydrogen atoms has been measured by Smallwood,[2] Senftleben and Riechemeier[3] and Steiner and Wicke.[4] Kassel[K] has summarized the results of these investigations. It seems fairly certain that the reaction takes place partly on the walls, although Senftleben and Riechemeier and Steiner and Wicke present some evidence to indicate that the wall reaction is not very significant, and partly as a trimolecular gas reaction. Opinion differs as to whether hydrogen atoms or hydrogen

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[1] The material in this paper comprises a portion of a thesis presented by I. Amdur to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June. 1932.

[2] Smallwood, THIS JOURNAL, 61, 1985 (1929).

[3] Senftleben and Riechemeier, Ann. Physik, 6, 105 (1930).

[4] Steiner and Wicke, Z. *physik.* Chem., Bodenstein Band, 817 (1931).

[5] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, pp. 177–180.

molecules, or both, act as third bodies in the trimolecular gas reaction.[6] Smallwood found atoms and molecules to be equally effective, Senftleben and Riechemeier found a much greater efficiency for collisions with atoms than with molecules and Steiner and Wicke concluded that atoms are relatively inefficient as third bodies, contributing at the most only ten per cent. of the effect attributed to hydrogen molecules. In view of the discrepancies reported, it seemed desirable to repeat certain portions of this work, using a large range of atomic hydrogen percentages. The effect of varying the total pressure through a twofold range was examined to determine, if possible, the influence of the wall. It is also shown that certain objections raised against the calorimetric method[4,7] are invalid.

Experimental

Apparatus and Procedure.—The apparatus was essentially that used by Smallwood[2] with the following modifications.

The rate of inflow of molecular hydrogen was determined from the reading of a calibrated ammeter when the rate of generation of hydrogen equaled the rate of pumping as shown by the constant levels of liquids in the limbs of the H-shaped generator. A high rate of pumping was secured by using a large four-jet mercury pump[8] connected in parallel with a single-jet pump. Three Hyvac pumps connected in parallel were used as fore pumps.

The temperature rise produced in the Dewar vessel, which served as a calorimeter, by the recombination of hydrogen atoms at the surface of the platinum catalyst was measured with a twenty-five junction copper–constantan thermocouple, the cold junction of which was immersed in a mush of ice and water in a Dewar vessel. The thermocouple was standardized against a Beckmann thermometer that had been calibrated by the U. S. Bureau of Standards. Between 20 and 30° the thermocouple voltage was a straight line function of the temperature with a value of 1006 microvolts per degree. Thermocouple voltages obtained during runs by means of a Leeds and Northrup Type K potentiometer were not converted to temperature rises since the heat capacity of the calorimeter was determined in terms of calories per millivolt rise of thermocouple voltage. Figure 1 shows a voltage–time plot for a typical run. The heat capacity of the calorimeter was determined at different positions along the recombination tube (with the discharge on and the platinum catalyst removed) for various rates of heating, corresponding to rates of heating observed during runs, by noting the increase in thermocouple voltage produced by passing a current through a constantan heating unit immersed in the calorimeter water, the energy input being measured potentiometrically.

Variations in pressure were obtained by decreasing or eliminating the heat input to the mercury pumps.

The walls of the recombination tube and discharge tube (both of Pyrex glass) were coated with sirupy phosphoric acid[7] made by dissolving C. P. phosphorus pentoxide in distilled water. As a result reproducible results were obtained when the apparatus was used continuously and runs at a given temperature were made in as short a time interval as possible.

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(6) For a discussion of the improbability of two atoms uniting to form a molecule as a result of a binary collision, see Boltzmann, "Gastheorie II," Leipzig, 1912: Polanyi, *Z. Physik*, **1**, 337 (1920); Herzfeld, *ibid.*, **8**, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); Jeans, "Dynamical Theory of Gases," fourth edition, Cambridge University Press, p. 195.

(7) Von Wartenberg and Schulze, *Z. physik. Chem.*, **B2**, 1 (1929).

(8) Ho, *Rev. Sci. Instruments*, **3**, 133 (1932).

Throughout the investigation the potential across the discharge tube electrodes was 6600 volts and the primary current of the transformer **was 32** amperes.

Results

The corrected thermocouple voltage increase was obtained by extrapolating the final cooling curve and the initial warming curve until the extrapolated lines intersected the ordinate drawn at the mid-point of the time abscissa which represented the duration of the discharge. The height of this ordinate gave the corrected voltage as shown in Fig. 1. The fraction of atomic hydrogen at any point along the recombination tube is given by

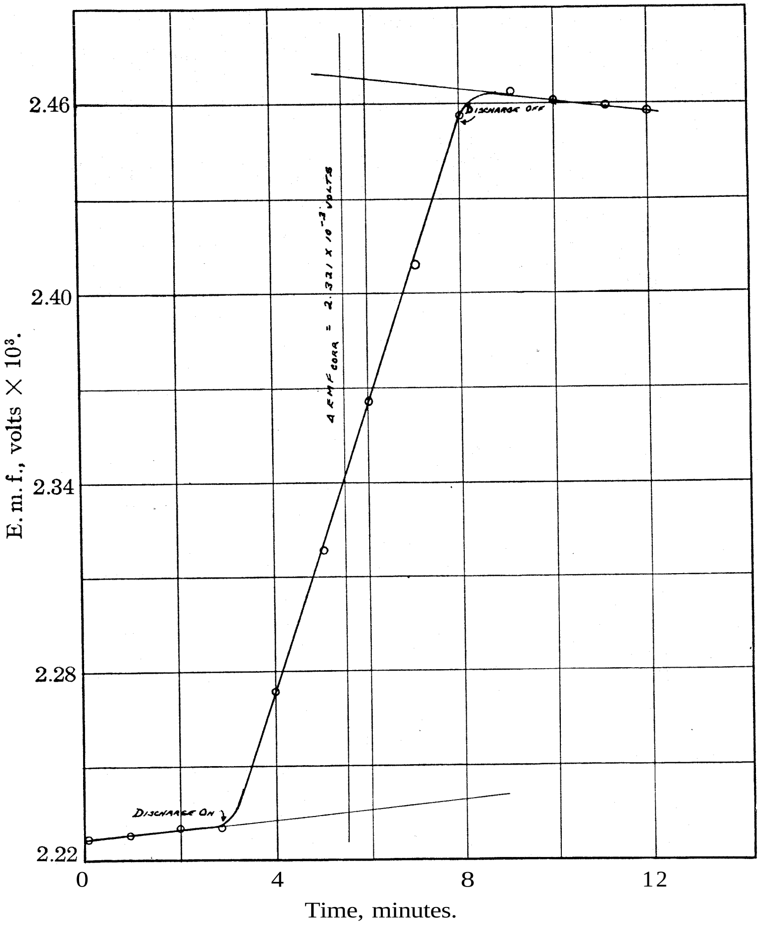

Fig. 1.—A voltage–time plot for a typical run.

$$\alpha = \frac{C\,\Delta \text{e. m. f.}_{\text{corr}}}{60 n_0 t\,\Delta H} \qquad (1)$$

where C is the heat capacity of the calorimeter in calories per millivolt,[9] ΔH is the heat of formation of one mole of molecular hydrogen from the atoms and was taken to be 102,800 calories per mole as reported by Richardson and Davidson,[10] and t is the time in minutes during which the discharge was on. The other symbols have the meanings designated in Table I. The runs in a single set in this table were all made in one day and fit a smooth curve well (Fig. 2).

TABLE I

MEASUREMENTS AT ROOM TEMPERATURE (25 ± 2°)

Internal diameter of recombination tube, 1.066 cm.; length ab,[a] 174 cm.

Set 1

$P_a{}^b = 0.375$ mm., $P_b = 0.162$ mm. Rate of flow of He $= n_0 = 0.881 \times 10^{-5}$ mole/sec

Distance from a to bottom of catalyst x, cm.	Time of discharge t, min.	E. m. f. (corr.) volts × 10³	Dissociation 100%
13.7	5	2.321	94.0
38.3	5	1.916	80.9
66.0	5	1.643	69.6
92.9	5	1.499	63.5
116.4	5	1.399	59.2

Set 2

$P_a = 0.466$ mm., $P_b = 0.245$ mm. $n_0 = 0.863 \times 10^{-5}$ mole/sec.

14.1	5	2.133	87.9
38.0	5	1.702	73.8
63.0	5	1.381	59.5
87.5	5	1.114	48.3
112.0	5	0.994	42.8

Set 3

$P_a = 0.648$ mm., $P_b = 0.485$ mm. $n_0 = 0.891 \times 10^{-5}$ mole/sec.

13.1	5	1.933	76.8
38.7	5	1.138	47.3
63.2	5	0.779	32.4
87.6	8	.883	23.2
112.4	10	.874	18.5

Set 4

$P_a = 0.802$ mm., $P_b = 0.682$ mm. $n_0 = 0.835 \times 10^{-5}$ mole/sec.

14.1	5	1.537	65.7
38.8	6	0.870	32.6
64.0	10	.874	19.6
88.7	14	.889	14.2
111.0	15	.719	10.6

[a] a and b are positions of the taps to the McLeod gage from the lower and upper ends of the recombination tube, respectively. [b] P_a and P_b are averages for separate runs in a set (measured at least twice during each run). The maximum deviation of the individual values from the recorded average was 3%.

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(9) When the calorimeter was quite close (10 to 15 cm.) to the discharge tube, this value was 110 calories per millivolt as compared to 115 calories per millivolt for all other positions along the recombination tube ab. The lower value is no doubt due to heat conduction from the discharge tube.

(10) Richardson and Davidson, Proc. Roy. *Soc.* (London), **A123**, 466 (1929).

To calculate reaction velocity constants for the various possible kinetic processes, a knowledge of the variation of pressure along the vertical recombination tube is necessary. Smallwood attempted to measure the change of pressure with distance by sealing in pressure taps at points along the tube and connecting the taps to the McLeod gage. He was unsuccessful, probably because of a catalytically active tube. We were more fortunate in our attempt. In Fig. 3 are shown the experimental values and smoothed curves for the variation of pressure along the recombination tube for the conditions corresponding to sets 1–4 of Table I. The pressure values as read from these curves check within 0.5 to 3% the values given by the approximate formula of Smallwood, namely

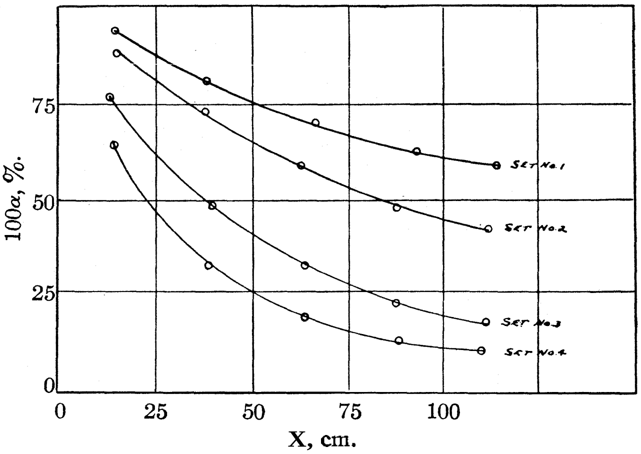

Fig. 2.—Percentage of atomic hydrogen *vs.* distance from discharge.

$$P = (P_a^2 - \beta x)^{1/2} \qquad (2)$$

and justify the assumption of viscous flow in the gas stream. The following derivation of the differential equation for the rate of decrease of hydrogen atoms is chiefly that used by Steiner and Wicke,[4] modified to take account of the variation of pressure along the tube. In the experiments of Steiner and Wicke this variation was small (about 10%) and consequently was neglected.[10a]

Assuming the absence of a wall reaction the variation of the number of hydrogen atoms with time may result from the following three processes (1) by recombination in triple collision

$$\left(\frac{\partial[H]}{\partial t}\right) = -k[H]^2([H] + [H_2]) \qquad (3)$$

(10a) For a criticism of the equation of continuity used by Steiner and Wicke *see* Amdur, *Phys. Rev.*, 43, 208 (1933).

(2) by the streaming of atoms from the discharge tube

$$\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_x = -\frac{\partial(V_x[\mathrm{H}])}{\partial x} \tag{4}$$

where v_x is the linear velocity (in centimeters per second) of the gas at the point x

$$V_x = \frac{n_0}{\pi r^2([\mathrm{H}_2] + 0.5[\mathrm{H}])} \tag{5}$$

(3) by diffusion of atoms

$$\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_x = \mathrm{D\ div.\ grad.\ [H]} \tag{6}$$

where D is the diffusion coefficient for atomic and molecular hydrogen.

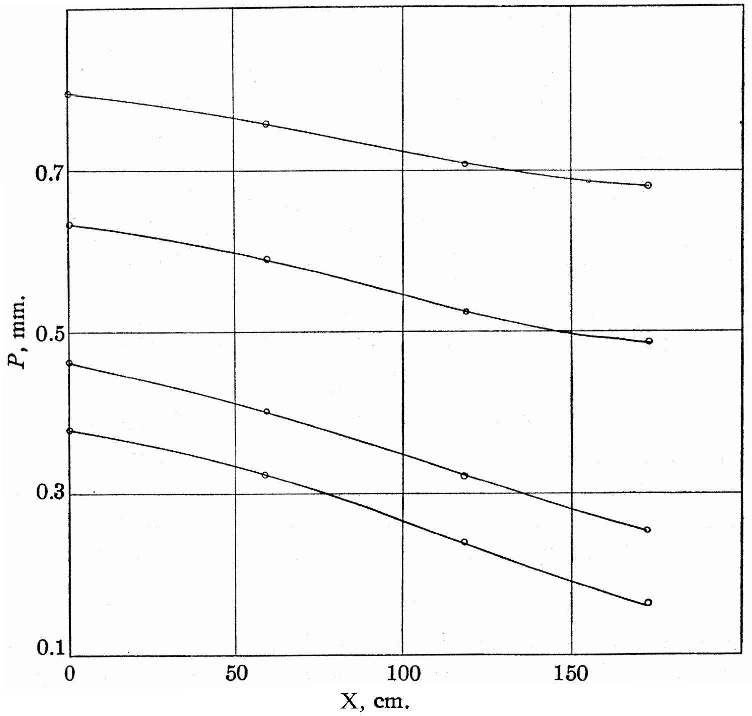

Fig. 3.—Pressure variation along the recombination tube.

Since the system represents a steady state in which $(\partial[\mathrm{H}]/\partial t)_x = 0$, we obtain from equations **3,** 5 and 6

$$D \text{ div. grad. } [\mathrm{H}] - \frac{\partial(V_x[\mathrm{H}])}{bx} - k[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H}_2]) = 0 \tag{7}$$

Assuming that the concentrations of atoms in a plane perpendicular to the tube ab at any given point is essentially constant, Equation 7 takes the form

$$D\frac{\partial^2[\mathrm{H}]}{\partial x^2} - \frac{\partial(V_x[\mathrm{H}])}{\partial x} - k[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H}_2]) = 0 \tag{8}$$

In order to obtain the value of k from experimentally determined data Equation 8 must be integrated. This is not readily accomplished by the ordinary methods for solving differential equations. If, however, one uses the differential equation directly by substituting slopes[11] determined graphically from experimental curves, and neglects the term $Db^2[\mathrm{H}]/\partial x^2$ (since its magnitude is only about 10^{-8} times that of $\partial(V_x[\mathrm{H}])/\partial x$), the expression for k becomes

$$k_1 = \frac{\dfrac{-\partial(V_x[\mathrm{H}])}{\partial x}}{[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H}_2])} = \frac{\dfrac{-\partial\left(\dfrac{n_0[\mathrm{H}]}{\pi r^2([\mathrm{H}_2] + 0.5[\mathrm{H}])}\right)}{\partial x}}{[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H}_2])} \qquad (9)$$

Equation 9 assumes that the wall effect is absent and that hydrogen atoms and molecules are equally efficient third bodies. If only hydrogen molecules are considered as possible third bodies, the above expression becomes

$$k_2 = -\frac{\dfrac{\partial\left(\dfrac{n_0[\mathrm{H}]}{\pi r^2([\mathrm{H}_2] + 0.5[\mathrm{H}])}\right)}{\partial x}}{[\mathrm{H}]^2[\mathrm{H}_2]} \qquad (10)$$

and for atoms as the only possible third bodies

$$k_3 = -\frac{\dfrac{\partial\left(\dfrac{n_0[\mathrm{H}]}{\pi r^2([\mathrm{H}_2] + 0.5[\mathrm{H}])}\right)}{\partial x}}{[\mathrm{H}]^3} \qquad (11)$$

In the above expressions the concentrations of atoms and molecules in moles per cc. are given by the relations

$$[\mathrm{H}] + [\mathrm{Hz}] = \frac{1332\,P}{RT} = P(5.42 \times 10^{-8})$$

$$[\mathrm{H}] = \frac{1332\,P}{RT}\,\frac{2\alpha}{1+\alpha} = \frac{P(5.42 \times 10^{-8})2\alpha}{(1+\alpha)}$$

$$[\mathrm{H}_2] = \frac{1332\,P}{RT}\,\frac{1-\alpha}{1+\alpha} = \frac{P(5.42 \times 10^{-8})(1-\alpha)}{(1+\alpha)}$$

where P, taken from the curves of Fig. 3, is expressed in mm. The values of R and T are 8.32×10^7 ergs per mole per degree and 296°K., respectively. Making the proper substitutions, Equations 9, 10 and 11 take the forms

$$k_1 = -\frac{\dfrac{\partial\alpha}{\partial x}\,2n_0(1+\alpha)^2}{\pi r^2\,P(5.42 \times 10^{-8})^3 4\alpha^2}$$

$$k_2 = -\frac{\dfrac{\partial\alpha}{\partial x}\,2n_0(1+\alpha)^3}{\pi r^2\,P(5.42 \times 10^{-8})^3 4\alpha^2(1-\alpha)}$$

$$k_3 = -\frac{\dfrac{\partial\alpha}{\partial x}\,2n_0(1+\alpha)^3}{\pi r^2\,P(5.42 \times 10^{-8})^3 8\alpha^3}$$

The units of the constants calculated in this manner are cc.^{2} mole^{-2} sec.$^{-1}$.

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[11] The use of slopes is probably more accurate than Steiner and Wicke's use of increments.

TABLE II

SUMMARIZED VALUES OF REACTION VELOCITY CONSTANTS

x	$\frac{\partial\alpha}{\partial x}$	a	P	$k_1 \times 10^{-15}$	$k_2 \times 10^{-15}$	$k_3 \times 10^{-15}$
25	0.00527	0.868	0.358	16.8	238	18.1
45	.00406	.773	.338	17.4	136	20.0
65	.00324	.702	.316	18.9	108	22.9
85	.00239	.647	.292	19.6	91	24.9
105	.00175	.606	.262	21.4	87	28.4
25	.00612	.808	.438	11.3	106	12.6
45	.00556	.689	.421	13.8	75	16.9
65	.00480	.581	.399	17.2	65	23.4
85	.00378	.494	.371	20.8	61	31.5
105	.00202	.441	.342	16.6	43	27.1
25	.0108	.597	.617	10.5	42	14.0
45	.00664	.426	.603	10.8	26.8	18.0
65	.00479	.316	.587	13.0	25.0	27.2
85	.00285	.239	.569	13.2	21.5	34.2
105	.00180	.194	.540	13.8	20.5	42.5
25	.0118	.452	.779	7.7	20.4	12.4
45	.00580	.287	.769	7.6	13.7	17.1
65	.00330	.196	.754	8.6	12.8	26.2
85	.00199	.146	.737	9.1	12.2	35.7
105	.00139	.113	.716	10.9	13.7	53.6

The constants in Table II were calculated for the reaction at 23°.

The accuracy of the experiments was limited by the reproducibility of results and the usual errors of calorimetry. Each of these sources it is estimated might contribute a maximum error of about 2%, making the combined effect about 4% at the most. The question as to whether all atoms collide with the catalyst[12] is settled definitely by the Einstein–Smoluchowsky formula for the time required for a particle in the center of a tube of radius r to diffuse to the walls. The formula is

$$t = \frac{3\pi r^2}{4Lc}$$

where L is the mean free path under existing pressure conditions and c is the mean molecular velocity at the temperature in question. Substitution of approximate values in the above expression shows that the time required for an atom in the flowing gas stream to hit the wall (or interior of the cylindrical catalyst) is small enough to insure complete recombination of all the atoms on less than 4 mm. of catalyst, if the catalyst is perfectly efficient. That such is actually the case was proved by Smallwood, who showed, in addition, that heat conduction from the discharge or transfer of energy by metastable molecules was negligibly small.

Discussion

The calorimetric method of measuring atomic hydrogen concentrations has been criticized by von Wartenberg and Schulze[7] and Steiner and Wicke[4]

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(12) Steiner and Wicke (Ref. 4) seem to feel that the calorimetric method yields low results.

on the ground that the abrupt recombination of atoms on the catalyst produces a pressure drop which in turn causes a sudden diffusion of the gas mixture at the catalyst. Although these authors claimed that the effects of diffusion are sufficient to vitiate results obtained by the calorimetric method, they made no attempt to calculate or determine the magnitude of the effect. It might be pointed out, in addition, that due to a slight lag in the transfer of heat to the calorimeter the catalyst is somewhat warmer than the gas stream below it. This would tend to warm the gas and cause additional diffusion. In order to determine definitely the contribution of these diffusion effects, pressure measurements were made at various points along the recombination tube with the discharge on, first with the catalyst present and then with the catalyst removed. It was found that the large linear velocities of the gas stream (9 to 12 meters per second) seem to overcome the pressure drops due to diffusion since pressures measured at various points along the tube were independent of the position of the catalyst in the tube and did not change when the catalyst was removed.

The presence of a wall reaction as a factor in the recombination of hydrogen atoms is still subject to question. Smallwood, using an apparatus whose walls were poisoned by water vapor introduced with the hydrogen, found that it was possible for the entire reaction to take place within 10^{-7} cm. of the wall if the reaction were represented as second order with respect to hydrogen atoms, the wall itself being the third body. He decided against a first order wall reaction since this would require an adsorbed layer of atomic hydrogen on the tube walls in spite of the fact that the tubing had not been baked out previously and was constantly covered with a water layer. Von Wartenberg and Schulze found that atomic hydrogen is reflected from aqueous films, not adsorbed. Moreover, a monomolecular reaction would give a wall process with a rate 10^5 times as great as the actual measured recombination rate.

Senftleben and Riechemeier, on the other hand, found a first order wall reaction whose magnitude varied from experiment to experiment but was always quite small. Steiner and Wicke do not regard these results as conclusive since, due to extremely low percentages of atomic hydrogen (less than 0.1%), only the very end portion of the reaction was being investigated. The statement of Steiner and Wicke that the wall reaction is negligible is based on the constancy of their trimolecular rate constants with respect to time and pressure. They present evidence to the effect that a wall reaction, if it existed, should be monomolecular, making impossible the obtaining of good trimolecular constants for the gas phase reaction if an existing wall effect is neglected. An additional argument given by these authors is the reproducibility of results with a tube coated with either water vapor or sirupy phosphoric acid.

In the case of our experiments, it was found that water vapor was not effective in producing a catalytically inert tube. The catalytic activity in this case was thought to be due to traces of metal rubbed off the brass chain supporting the catalyst. Coating the tube with sirupy phosphoric acid and replacing the brass chain by a less corrosive German silver chain produced an apparatus in which reproducible results could be obtained when runs were not taken at too widely separated intervals. That a wall reaction is present nevertheless in this investigation is indicated by the drift of the constants. The contribution to the total rate, however, is probably small, inasmuch as the values of our constants do not differ materially from those of Steiner and Wicke, who used a recombination tube of much larger diameter. Furthermore, the values of our constants obtained from experiments in a tube coated with sirupy phosphoric acid are in good agreement with those of Smailwood obtained in a tube coated with water vapor.

In regard to the gas phase reaction, the nature of the apparent rate constants in the present investigation indicates a more complicated mechanism than that proposed by Steiner and Wicke, who claim that only hydrogen molecules are significantly effective as third bodies in the reaction. Their statement is based on the fact that the rate constants for the reaction between two atoms and a molecule have values in all experiments of $9 \pm 2 \times 10^{15}$ cc.^{2} mole^{-2} sec.$^{-1}$, while the rate constants for the reaction in which molecules and atoms are regarded as equally efficient third bodies vary considerably and show definite drifts. However, an inspection of the data of Steiner and Wicke indicates that their accuracy cannot be high, certain experimental points deviating by 70% from the smoothed curves drawn. Further uncertainty is introduced by the calibration of the intensity of the H_α line, so that the calculated rate constants depend to some degree upon what seems to be an arbitrary selection of experimental values and the constancy found must be partly fortuitous. In a recent theoretical article[13] Steiner considers the homopolar valence binding forces acting between two hydrogen atoms and the probability of resonance interchange between this atom pair and a hydrogen molecule, and concludes that this process could be mainly responsible for the combination of hydrogen atoms, in agreement with the experimental results of Steiner and Wicke. Kimball[14] has pointed out that there is an equally probable way in which this triple collision could take place, first a collision between a hydrogen atom and a hydrogen molecule followed by a collision with the second hydrogen atom. A kinetic study cannot distinguish between these two mechanisms since both are expressed formally by $d(H)/dt = -k(H)^2(H_2)$; only the calculation of kinetic theory diameters is affected.

That a triple collision of three hydrogen atoms leading to the forma-

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(13) Steiner, Z. *physik. Chem.*, **B15**, 249 (1932).

(14) Kimball, THIS JOURNAL, 54, 2396 (1932).

tion of a hydrogen molecule does not involve an energy of activation is indicated by Eyring's[15] potential energy diagram for this system. Our results indicate that both types of triple collisions contribute to the formation of hydrogen molecules. The constants for the reaction involving two atoms and a molecule, k_2, tend to reach a constant value only in regions of high molecular (low atomic) hydrogen percentages, while the constants involving three atoms, k_3, drift in the opposite direction. This is particularly noticeable in the runs where the atomic hydrogen percentage varied four- and six-fold (see Sets Nos. 3 and 4, Tables I and II), indicating the presence of two reactions, namely, collisions of two atoms and a molecule and collisions of three atoms, the former predominating at low atomic hydrogen percentages and the latter at high atomic hydrogen percentages. The fact that the variation of k ~ ,which involves equally efficient collisions of two atoms with either a third atom or a molecule, is less than that of k_2 or k_3 tends to confirm the presence of two reactions. These one to one efficiencies may be considerably varied (ratio of atom efficiency to molecule efficiency may be as small as one to four) without appreciably changing the values of k_1. One may conclude, therefore, that the results of this investigation cannot be represented by Steiner's mechanism alone since the best trimolecular constants are obtained only when the effects of both hydrogen atoms and molecules as third bodies are taken into account, an efficiency for molecules four times that for atoms being permissible.

Some measurements of the reaction velocity have been made in the temperature range 194 to 372°K. We hope to discuss these measurements in an article now in preparation.

We wish to extend our sincere thanks to Professor **A.** E. Ruark of the Department of Physics, University of Pittsburgh, for his generous aid and advice offered throughout the course of this investigation.

Summary

1. Objections raised against the calorimetric method for determining percentages of atomic hydrogen in an atomic-molecular hydrogen gas mixture have been discussed. Diffusion due to the large pressure drop caused by recombination of atoms on the catalyst and by the heating of the gas stream by the warm catalyst seems to be minimized by the large linear velocities of the gas stream, since pressure measurements cannot detect the effects of such a diffusion.

2. There is a possibility of the existence of a wall reaction in the recombination of hydrogen atoms, but the facts that the rate constants for the reaction between three hydrogen atoms at high atomic hydrogen percentages do not vary greatly with pressure and that consistent results are ob-

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[15] Eyring, THIS JOURNAL., 53, 2537 (1931); *Chem. Rev.*, 10, 103 (1932).

tained in different apparatus under different conditions of the wall surface indicate that the contribution of the wall reaction to the total rate is small.

3. Both atoms and molecules can act as third bodies with an allowable greater efficiency for molecules.

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Azeotropic Hydrobromic Acid Solutions at Pressures of 100 Mm. to 1200 Mm.

BY WALTER D. BONNER, LYMAN G. BONNER AND FRANCIS J. GURNEY

Some years ago we undertook as a part of the research program of this Laboratory a careful study of the boiling points, compositions, and densities of the azeotropic or "constant-boiling" acid solutions. The present paper represents the second acid thus far studied, the data on hydrochloric acid having been already published.[1]

Preparation of Hydrobromic Acid.—Two different methods were used in preparing the hydrobromic acid. The simpler was that of reduction of bromine by sulfur dioxide in the presence of sufficient water to give a solution of approximately constant boiling composition. This solution when freed of excess sulfur dioxide contained, of course, the equivalent amount of sulfuric acid, but the more volatile hydrobromic acid was readily removed from this by distillation. After this first distillation the HBr solution was treated with an excess of solid barium bromide and again distilled. The sulfate-free acid was then repeatedly redistilled, rejecting the first and the last portions, until a solution was obtained which was constant boiling at atmospheric pressure, and which also was free from any analytically significant impurity. In some cases we used bromine which we had carefully purified by the method of Baxter[2] while in other cases we used bromine of "reagent" quality, without further purification. The final acid solutions could not be distinguished.

The second method of preparation of hydrogen bromide solutions was that of direct synthesis from the elements. The hydrogen bromide solutions prepared by this method were indistinguishable from those prepared by the simpler method. Most of our acid was consequently made by the first method.

Preparation of Azeotropic Solutions.—The methods were much the same as those used previously for preparing constant boiling hydrochloric acid.[1] Due, however, to the particularly corrosive character of

(1) Bonner and Branting, THIS JOURNAL, 48, 2093 (1926); Bonner and Titus, *ibid.*, 52, 633 (1930); Bonner and Wallace, *ibid.*, 52, 1747 (1930).

(2) Baxter, *ibid.*, 28, 1325 (1906).

hydrobromic acid it was found necessary so to prepare the samples that neither the vapor nor the liquid acid came in contact with any material but glass. The apparatus consisted of a 250-cc. Claissen flask with a thermometer sealed into one neck. The other neck was left open for filling. The distilling arm which was on the closed neck of the flask was sealed to a condenser tube of 6 mm. internal diameter. This was connected to the 250-cc. receiver as well as to the pressure control apparatus by means of ground glass joints. The distilling flask rested in a hole 3 cm. in diameter in a heavy asbestos plate, and the double neck of the flask was heavily insulated by wrappings of asbestos cord. The pressure control apparatus and the barometer have already been described.[1] The samples were prepared at the uniform distillation rate of approximately 3 cc. per minute. A bundle of fine capillary tubes served to prevent bumping. When first we began studying these solutions we frequently found them colored markedly red. On distillation this red color would accumulate in the residue, where it could be shown to be due to the presence of iron. This we eliminated by filtering through absorbent cotton all air or other gas which went into the pressure control apparatus. To exclude the possibility of air oxidation of hydrogen bromide we prepared all the azeotropic solutions in an atmosphere of carbon dioxide. We have also preserved our samples sealed under carbon dioxide. In preparing the apparatus for operation, about 200 cc. of hydrobromic acid solution, constant boiling at atmospheric pressure, was charged into the Claissen flask through the open neck. Connection was then made to the receiver and to the pressure control apparatus, and carbon dioxide (from a commercial cylinder) passed through the entire apparatus, until the air was well swept out. The open neck of the flask was then sealed off, and the desired pressure obtained, either by pumping out carbon dioxide, or by building up carbon dioxide pressure from the cylinder. This pressure having been established, the sample was boiled until about two-thirds of it had distilled over, the thermometer sealed in the neck of the flask indicating a steady boiling temperature. Distillation was then stopped, the receiver emptied, cleaned and dried, and the apparatus reassembled. After refilling the apparatus with carbon dioxide, and reestablishing the pressure, distillation was begun anew and continued until about one-half the remainder had distilled over.

Analytical Methods.—The composition of the azeotropic solutions was determined gravimetrically, weighing the bromine as silver bromide. All usual precautions were taken, and all significant corrections applied. Densities were determined by use of a pycnometer, adjusted in a thermostat at 25 ± 0.05°. The volume of the pycnometer was 5.7865 cc.

Boiling points were determined by means of the platinum resistance thermometer and boiling point apparatus previously described in the work on hydrochloric acid.[1] About 10 g. of platinum tetrahedra were used to facilitate boiling without bumping.

Precision of Data.—The data presented on the composition of the constant boiling acids are in practically all cases means of the compositions of distillate and of residue. The maximum deviation from the mean is in general about 0.05% and in no case exceeds 0.1%. Correction to vacuum has not been made, as it falls outside this limit of precision. Calibrated weights were used, and any significant corrections applied. Densities as given are also the means of the densities of distillates and of residues. These have been corrected to vacuum, and for weight calibrations, and are reproducible to about 0.01%. The deviation between the densities of *a* distillate and of the corresponding residue was, however, generally greater than this, being at the most about 0.05%. This corresponds to a difference in composition between distillate and residue of at most 0.1%. It has already been pointed out[3] that density determinations constitute the most sensitive method of ascertaining whether a given distillate is really "constant boiling."

Pressures were measurable to 0.5 mm. or less and reproducible to 1 mm. or less. Barometric readings have been constantly compared with those of the local Weather Bureau. The boiling points as given are reproducible to about 0.02". The data all are assembled in Table I.

TABLE I

Pressure in mm.	B. p. in °C.	Density at 25°	Comp. in HBr
100	74.12	1.5116	49.80
200	90.35	1.5030	49.28
300	99.91	1.4961	48.83
400	107.00	1.4908	48.47
500	112.94	1.4866	48.19
600	117.82	1.4832	47.95
700	122.00	1.4802	47.74
800	125.79	1.4775	47.56
900	129.13	1.4752	47.40
1000	132.12	1.4733	47.27
1100	134.80	1.4716	47.14
1200	137.34	1.4700	47.03

The data on constant boiling hydrobromic acid have been well summarized by Ewing and Shadduck.[4] So far as we are aware, the data of Van Valkenberg and Bischof[5] are the only ones which have appeared since. Unfortunately the data are not very consistent. Disregarding the older ones, those which have accumulated since 1923 are still not satisfactory, as the following exhibit shows.

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(3) Hulett and Bonner, THIS JOURNAL, 31, 391 (1909); Foulk and Hollingsworth, *ibid.*, 45, 1220 (1923).

(4) Ewing and Shadduck, *ibid.*, 47, 1901 (1925).

(5) Van Valkenberg and Bischof, *J. Colorado-Wyoming Acad. Sci.*, 1, 25 (1929).

Observer	Pressure	Boiling point, °C.	Composition, % HBr
Carrière and Cerveau[6]	760 mm.	126	47.5
Ewing and Shadduck	760 mm.	125	47.79
Bonner, Bonner and Gurney	760 mm.	124.3	47 63

These represent the most precise data available for a pressure of 760 mm. Those of Carrière and Cerveau cannot be regarded as of high precision as the composition was determined by titration. Ewing and Shadduck, on the other hand, made very careful gravimetric analyses, but apparently used no criterion to show that they were dealing with actually azeotropic solutions. The same criticism is to be made of Van Valkenberg and Bischof's data. Their work was done at pressures between 630 and 700 mm., but they neglected to check the composition of the residue to show that it was the same as that of the distillate. The four pressure–composition points reported by Van Valkenberg and Bischof do not fall on a smooth curve, and the best curve which can be drawn through them has a very much steeper slope than has our curve at any point. Their boiling points, however, fall very close to our boiling point curve.

We believe that our data are the most consistent yet presented on azeotropic hydrobromic acid solutions. They are not so precise as those available on hydrochloric acid solutions.

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[6] Carrière and Cerveau, *Compt. rend.*, 177, 46 (1923).

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

The Photostationary States of Some Geometrically Isomeric Acids

BY A. R. OLSON AND F. LYTH HUDSON[1]

Over twenty years ago, Stoermer[1a] showed that many pairs of stereoisomers yield equilibrium mixtures on illumination with ultraviolet light. He showed further that in such a photochemical equilibrium the less stable form was present in the larger amount, thus proving that light does not act merely as a catalyst in hastening thermal equilibrium. The photostationary state of maleic–fumaric acids was studied in greater detail by Kailan.[2] Using a quartz mercury arc without filters, he found that the steady state (about 75% maleic acid) was slightly affected by concentration, but was not affected by the substitution of glass for quartz containers. This reaction was studied further by Warburg,[3] who measured the quantum efficiencies of light at the wave lengths 2070, 2530 and 2820 Å. Vaidya[4] extended the range to 3130 Å., and in addition determined the quantum efficiencies of light of this wave length for producing inversion of citraconic, o-coumaric, cinnamic and isocinnamic acids. Stoermer had found that solutions of mesaconic acid in methyl alcohol are scarcely changed into citraconic acid on illumination. Vaidya quotes this result, but does not say whether or not he tested it in aqueous solution.

Olson,[5] in a theoretical paper, treated stationary states of this kind with the aid of potential energy diagrams. Figures 1 and 2 are taken from this paper. Figure 1 represents a plot of the potential energy of a molecule against the angle φ, through which one-half of a molecule is twisted relative to the other about the double bond as axis, starting with $\varphi = 0$ for the cis molecule. The lower curve is the type to be expected for an unexcited molecule. It is assumed that excitation removes an electron to such a distance that the effect of the double bond disappears. The upper curve is, then, the simplest type to be expected for an excited molecule. The height of the top above the trough of this curve is, then, the heat of the transition, when one molecule changes into the other. The shape of these curves is not known from experimental data, but for the purpose of this discussion of a simple case it was assumed that the upper curve had the equation

$$V = A - k \sin^2 (\varphi/2)$$

With the above assumption regarding the potential in the upper state, the Schroedinger equation reduces to the Mathieu equation, for which

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(1) Commonwealth Fellow, University of California.

(1a) Stoermer, *Ber.*, 44, 637 (1911).

(2) Kailan, *Z. physik. Chem.*, 87, 333 (1914).

(3) Warburg, *Sitzb. preuss. Akad. Wiss., Physik.-math. Klasse*, 33, 960 (1919).

(4) Vaidya, Proc. Roy. Soc. (London), [A] 129, 299 (1930).

(5) Olson, Trans. *Faraday Soc.*, 27, 69 (1931).

solutions are known. One may then calculate the ψ function for a level such as B″B″ in the upper state. If this is done, it is found that the probability (as measured by ψ^2) of finding the molecule in the upper state between the angles $-\pi/2$, $\pi/2$ is very much greater than that of finding it between $\pi/2$, $3\pi/2$; that is, it is in the *cis* state for the greater part of the time. If this is repeated for various energy levels, one obtains a graph such as Fig. 2 for the ratio of *cis* to *trans* to be expected at the stationary

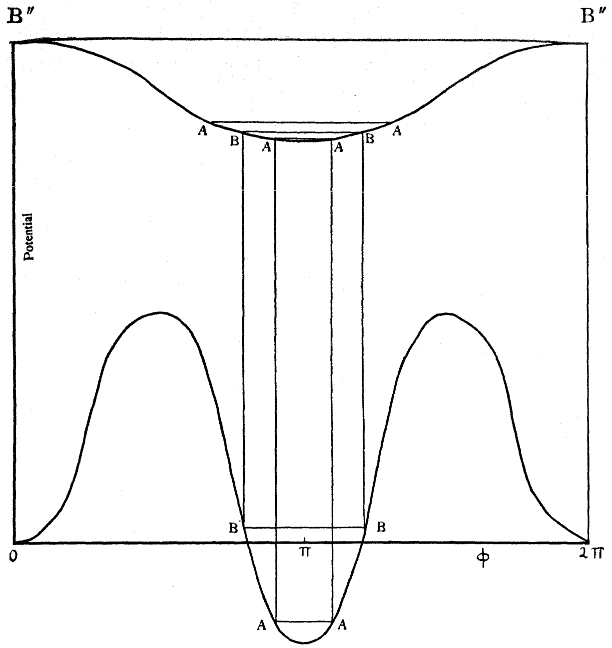

Fig. 1.

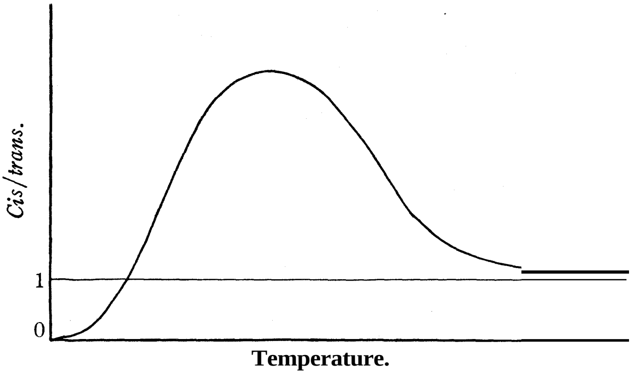

Fig. 2.

state at various temperatures. The same result is obtained, whether one considers the problem from the point of view of the Schroedinger equation for a torsional vibrator, or from that of a mechanical model. Thus, mechanically, this means that the fraction of the total time that a pendulum is in the region of high potential energy increases with the amplitude of the swing until the pendulum can make a complete revolution. If the energy of the pendulum is increased still further, the ratio of the velocity of the pendulum in the upper half of the revolution to that in the lower half of the revolution approaches unity and therefore the ratio of the times spent in these two configurations approaches unity. In this article no account was taken of differences in absorption coefficients of the two isomers, and so the conclusions applied only if the absorption coefficients were equal.

We shall now discuss a quantity which will replace the ratio of the concentrations in cases where the coefficients are not equal. Consider **a** thin slice dx of solutions of *cis* and *trans* acids, whose molecular absorption coefficients and concentrations are, respectively, α_1, α_2, C_1, C_2. Suppose the slice is illuminated in the direction of x by monochromatic light of intensity **J** quanta per second over the area of the slice. We will define p as the mean probability that a molecule of either kind, which has absorbed a quantum, will return to the *cis* state on deactivation. Then $1 - p$ is the probability that it will return to the *trans* state.

For this case Beer's law may be written

$$-\frac{1}{J}\cdot\frac{\mathrm{d}J}{\mathrm{d}x} = \alpha_1\cdot C_1 + \alpha_2\cdot C_2$$

The number of quanta absorbed in this slice is

$$-\,dJ = J(\alpha_1\cdot C_1 + \alpha_2\cdot C_2)\,\mathrm{d}x$$

The number returning to the *cis* state per second will be

$$pJ(\alpha_1\cdot C_1 + \alpha_2\cdot C_2)\,\mathrm{d}x$$

At the steady state, this must be equal to the number of *cis* molecules absorbing in one second, which is

$$J\cdot\alpha_1\cdot C_1\,\mathrm{d}x$$

$$J\cdot\alpha_1\cdot C_1\,\mathrm{d}x = pJ\,(\alpha_1\cdot C_1 + \alpha_2\cdot C_2)\,\mathrm{d}x$$

$$\alpha_1\cdot C_1 = p(\alpha_1\cdot C_1 + \alpha_2\cdot C_2)$$

Similarly for the *trans* molecules

$$\alpha_2\cdot C_2 = (1 - p)(\alpha_1\cdot C_1 + \alpha_2\cdot C_2)$$

$$\frac{p}{1 - p} = \frac{\alpha_1\cdot C_1}{\alpha_2\cdot C_2}$$

Further, suppose the quantum efficiencies of the two acids, expressed as molecules isomerized per quantum absorbed, are Θ_1, Θ_2. There will be formed per second $\Theta_1\cdot J\alpha_1\cdot C_1\cdot\mathrm{d}x$ molecules of *trans* from *cis* and $\Theta_2\cdot J\cdot\alpha_2\cdot C_2\cdot\mathrm{d}x$ molecules of *cis* acid from *trans*. At the steady state these must be equal.

$$\frac{\Theta_2}{\Theta_1} = \frac{\alpha_1\cdot C_1}{\alpha_2\cdot C_2} = \frac{p}{1 - p}$$

The above equations define p in terms of experimental quantities and make no assumptions as to what actually happens in the upper state. We may now replace C_1/C_2 in Olson's paper by $p/(1 - p)$ and apply the argument to isomers, whatever the ratio of the absorption coefficients may be.

Both α_1/α_2 and $p/(1 - p)$ may vary with wave length, so it is desirable that monochromatic light should be used. If continuous radiation is used, light of some frequencies may be almost completely absorbed in a very short distance (the first 0.1 mm.), while other frequencies will get farther into the solution. Thus, if there is no diffusion, one may well get a different photostationary composition in each layer. The actual result obtained will vary with the size and shape of the containing vessel and the time of exposure. Thus, a photostationary state measured with general illumination is devoid of any meaning. In the case of fumaric and maleic acids the absorption coefficients are nearly equal over the whole spectrum, so that here $p/(1 - p) = C_1/C_2$, and this difficulty does not arise. This probably explains why Kailan[2] obtained the same photostationary state in quartz and glass vessels. In the other cases investigated, α_1/α_2 varies rapidly with wave length, so filters were used to get the nearest possible approach to monochromatic light.

Experimental

Preparation of Materials.—The less stable of two stereoisomeric acids is usually much more soluble in common solvents than the more stable; hence, it is unreliable to purify maleic, citraconic, or cis-cinnamic acid merely by crystallization. Maleic acid, for example, is about a hundred times as soluble in water as fumaric, so repeated recrystallization from water will produce a product containing one per cent. of fumaric acid.

Fumaric acid from the laboratory supplies was purified by three crystallizations from hot water. The product melted at **285"** in a sealed tube. Maleic acid was purified by a method due to Terry and Eichelberger. It melted at **134.5".** As the value given in the literature is **131°**, the acid was again converted into the anhydride and the process repeated. It still melted at 134.5°, which appears to be the correct melting point. Vaidya[4] also gives 134° as the melting point of his acid.

Ordinary trans-cinnamic acid was recrystallized from hot water and melted at **133.4".** Cis-cinnamic acid was made by a method due to Stoermer.[6] The acid melted sharply at 58.3°. **A** second preparation melted at **67.8".** According to Beilstein's "Handbuch der organischen Chemie," there are three different crystalline forms of cis-cinnamic acids, melting at 42, 58 and 68". The last is the most stable, but all three are considered to be the same in solution.

Kahlbaum's citraconic and mesaconic acids were used. They were purified in the same way as fumaric and maleic acids, except that the citraconic anhydride could not be crystallized and was distilled instead.

Conductivity Measurements.—In the cases examined $M/200$ solutions of the cis acids have conductivities about twice as great as the corresponding solutions of the trans acids. Mixed solutions are therefore readily analyzed by means of their conductivities. This method has been used by other investigators. The cell was kept in a water thermostat and connected to the rest of the circuit by twelve-foot leads, which

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(6) Stoermer, *Ber.*, 42, 4866 (1909).

were shielded. With this circuit, a change in resistance of **4** parts in **10,000** could readily be measured.

Two Pyrex conductivity cells were used, each holding about **6** cc. of solution and having platinum black electrodes about **1** cm. square and **0.5** cm. apart. To facilitate filling and emptying, two tubes were sealed on, provided with glass stoppers and bent in the same way as those on the absorption cell F, Fig. **3.** The cells were standardized by means of decimolar potassium chloride, made up according to the method of Parker and Parker,' whose value for the specific conductivity was used. This was not an essential part of the method, but was done so that the conductivities of the solutions might be compared with published values.

The solutions were to be used at different temperatures, so that a definition of concentration by volume was undesirable. They were therefore made up by weight. directly in the Jena glass bottles in which they were kept. Conductivity water, distilled from alkaline permanganate, was used.

Table I gives the values obtained for the molecular conductivities compared with those of other authors. For this the solutions were assumed to be 0.005 molar; the error produced by this is less than that of the uncalibrated instruments.

TABLE I

MOLECULAR CONDUCTIVITIES

Acid	Molarity	Molecular conductivities Obs.	Vaidya[4]	Ostwald[8]	Rivett Sidgwick[9]	White Jones[10]	Bjerrum[11]
Fumaric	0.005	136	136	134			
Maleic	.005	294	287	288	288		
Mesaconic	.005	122	126	123.5		117	
Citraconic	.005	211	214	208	204	222	
T.-cinnamic	.003	39.6	39.7	39			
C.-cinnamic	.003	72.8	74				72.5

Except for Vaidya's results, which were for the same concentrations as those used by us, the above figures were obtained by graphical interpolation.

Measurement **of** Photostationary States.—The quantum efficiencies of the isomeric changes are low (see Table VIII), so it is not desirable to start with a pure acid and illuminate it until it reaches a steady state. The steady state is found by making up a mixture close to it in composition, filling a conductivity cell with part of it and illuminating part. The change in the bridge reading on illumination may then be found. The quartz illumination cell held about **2** cc. more than the conductivity cells, so one of the latter could be filled with the exposed solution. The mixtures were made up from the stock solutions by means of calibrated burets. The change in bridge reading was plotted against the composition of the solution; when about three points were obtained on each side of zero change, a mean curve was drawn through them, the point of zero change giving the composition at the photostationary state.

Volmar[12] has stated that maleic, fumaric, citraconic and mesaconic acids are de-

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(7) Parker and Parker, THIS JOURNAL, 46, 312 (1924).

(8) Ostwald, *Z. physik. Chem.*, 3, 369 (1889).

(9) Rivett and Sidgwick, J. *Chem. Soc.*, *97*, 1677 (1910).

(10) White and Jones, Am. *Chem.* J., *44*, 175 (1910).

(11) Bjerrum, Ber., 43, 571 (1910).

(12) Volmar, *Compt.* rend., 181, 467 (1924).

composed by light with the evolution of carbon dioxide and the formation of acids of the acrylic acid series. This is denied by Vaidya.[4] Oxalic, formic, lactic and several other acids are decomposed in a similar way, according to Pierce and Morey.[13] It was desirable, therefore, to see whether any such reaction took place to an extent sufficient to interfere with determinations of the photostationary states. Mixtures of approximately the same compositions as the photostationary mixtures were exposed at 90° for two hours to the unfiltered mercury arc radiation. After cooling, 5 cc. of the solution was titrated with $m/200$ baryta water in a current of carbon dioxide-free air. No measurable change was detected for any of the acids used. Thus, any actual change must be less than 1% for this exposure, or less than 0.25% for half an hour's exposure, which was usually used in determinations This method would not show any reaction involving no change in the total acid concentration.

Source of Light, Filters, etc.—A Cooper–Hewitt mercury arc was used in all experiments. To get the greatest possible intensity, it was backed by a bright aluminum reflector, calculated to bring the light to an approximate focus at the quartz cell.

Two filters were used: a chlorine filter for the 2536 Å. line, and a potassium chromate one for the two lines near 3130 Å. The chlorine filter has been described by Oldenberg.[14] A stout quartz bulb, 5.5 cm. in diameter, was sealed onto a graduated Pyrex tube, into which some liquid chlorine was distilled while it was cooled in liquid air. The system was then evacuated and sealed off, and spectrograms taken with the chlorine at various pressures, controlled by altering the temperature of the graduated tube. Four and one-half atmospheres was chosen as the best pressure. The seal was broken and chlorine was distilled off until enough of the liquid remained to produce this pressure in the bulb. The chlorine was then condensed in the bulb, the air pumped off and the bulb sealed. As the vessel was not optically plane, it was not possible to determine its transmission experimentally, but this may be calculated approximately from the results of von Halban and Siedentopf.[15] In the course of some measurements of absorption coefficients, to be described later, spectrograms of the mercury arc were taken with screens of different transmissions. From these the relative intensities of the unfiltered 2650 and 2536 groups of lines were approximately computed as 1:1.9. These two lines are transmitted by the chlorine to the extent of 10 and 64%, respectively. By multiplying the two ratios, we find the effective light transmitted by the filter is 92% of 2536 and 8% of 2650. The only other light transmitted appreciably has a wave length greater than 4000 and no photochemical effect. These figures are very approximate, as the absorption of the irregular quartz surfaces is not taken into account. Also the 'photographic effect of this light is not uniform.

In the neighborhood of 3100 Å. the effect of light on a photographic plate is fairly uniform for different wave lengths. The transmission of the potassium chromate filter (made of 2.5 cm. of $m/2000$ K_2CrO_4) and the intensities of the lines transmitted are given in Table II. They were determined by absorption measurements and may be taken as accurate within 5%.

TABLE II

Lines	3341	3130	3020	2967
Relative intensities	0.18	1.74	0.49	0.29
Percentage of line transmitted by filter	6.0	43.7	21.6	6.0
Relative amounts of energy transmitted	1.2	85	11.9	1.9

The arrangement used for the chlorine filter is shown in Fig. 3. The chlorine in the bulb A is fitted into a Bakelite tube B, with rubber washers above and below. The side

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(13) Pierce and Morey. THIS JOURNAL, 54, 467 (1932).

(14) Oldenberg, *Z. Physik*, 29, 328 (1924).

(15) Von Halban and Siedentopf, Z. *physik*. Chem., 103, 80 (1922)

tube on the bulb projects through a slot in B. The lower end of B is closed by a plane quartz window D, which is clamped down tightly onto a rubber washer by the Bakelite flange E. E is held on by nuts on three threaded brass rods (not shown in the figure), screwed tightly into B. The circular quartz cell F is 0.5 cm. thick and holds 8 cc. It is held, for convenience, between two brass flanges G, connected together with three screws. They have holes bored to fit the brass rods projecting from E, and are slipped over these and screwed on with wing nuts, so that the cell is about half a cm. below D. When a weakly absorbing solution was being used, F was backed by an aluminum reflector, so as to double its effective length. The upper part of B has a flange resting on a metal support, by means of which the filter and cell are hung in a thermostat, so that cooling air could be circulated around A when runs were made above room temperature. Water was convenient for use in the thermostat, as it transmits ultraviolet light. At temperatures above 60° it required continuous replenishing to balance evaporation.

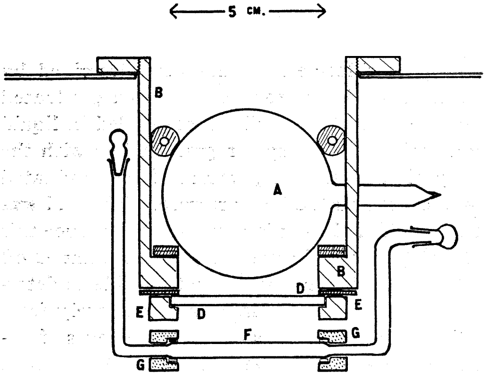

Fig. 3.

When the potassium chromate filter was used, it was contained in a vessel similar to F, but 2.5 cm. thick. This was hung above F from the top of the thermostat by means of a wire frame. The box containing the mercury arc was brought immediately above the top of the thermostat. The temperature was controlled to one-tenth of a degree by a toluene–mercury regulator.

Cinnamic acids have fairly high quantum efficiencies and readily gave results with both filters With the other acids, however, the change was very slow. Results with citraconic and mesaconic acids were obtained with the potassium chromate filter, but are approximate only to one or two per cent. Maleic and fumaric acids were investigated without any filters,

The Measurement of Absorption Coefficients.—The absorption coefficients were measured by a photographic method which Mr. N. S. Bayliss has been using in this Laboratory in connection with another problem. Since the details of the method are to be published soon, it will suffice to note that by this method the accurate results of Halban and Siedentopf on the absorption by chlorine were checked within 2%.

The values obtained for the extinction coefficients are given in Tables III and IV. It will be observed that the values of the ratio ϵ *cis*/ϵ trans vary less than the values of the coefficients themselves. This may be due to the very rapid change of ϵ with wave length, which rises as much as 1% per Angstrom unit. A small change in the setting of the microphotometer is then liable to cause a large change in the value obtained for ϵ. The starred values in the tables were obtained from extrapolations on the blackening curves, and are not reliable.

Results for Photostationary States.—0.005 M solutions were used for maleic, fumaric, citraconic and mesaconic acids, and 0.003 M solutions for the two cinnamic acids. In the last case, readings could not be taken below 15°, as the *trans*-cinnamic acid crystallized. For fumaric and

TABLE III

EXTINCTION COEFFICIENTS

Maleic, Fumaric, Citraconic, Mesaconic Acids

Plate	Wave length, Å.	Thickness, cm.	Acid	Concn., mole per liter	$\log \frac{J_0}{J}$	ϵ	$\frac{\epsilon\ cis}{\epsilon\ trans}$
9	3130	5.46	mal.	0.01022	0.410	7.41	0.954
			fum.	.00996	0.418	7.69	
9	3020	5.46	mal.	.01022	1.08	19.4	0.84*
			fum.	.00996	1.25*	23*	
10	3130	6.99	mal.	.01022	0.504	7.05	
			fum.	.00996	.482	6.90	1.02
11	3130	8.49	mal.	.01022	.653	7.52	
			fum.	.00996	.635	7.30	1.004
19	3130	9.00	mal.	.00991	.716	8.02	0.974
			fum.	.00999	.739	8.23	
18	3020	2.96	mal.	.00991	.568	19.4	.93
			fum.	.00999	.618	20.9	
18	3020	2.96	citrac.	.05303	.464	2.95	.215
			mesac.	.02022	.818	13.7	
9	3020	5.46	citrac.	.05303	.850	2.93	.25*
			mesac.	.01995	1.3*	12*	
9	3130	5.46	citrac.	.05303	0.291*	1.01*	.287*
			mesac.	.01995	.382	3.51	
10	3130	6.99	citrac.	.05303	.353	0.952	.289
			mesac.	.01995	.459	3.29	
11	3130	8.49	citrac.	.05303	.448	0.994	.287
			mesac.	.01995	.588	3.47	
19	3130	9.00	citrac.	.05303	.494	1.035	.308
			mesac.	.02022	.606	3.36	

The accompanying values of the ratio were taken as averages

Wave length	$\frac{\epsilon\ mal.}{\epsilon\ fum.}$	$\frac{\epsilon\ citrac.}{\epsilon\ mesac.}$
3130	1	0.29
3020	0.93	0.22

maleic acids, unfiltered light was used and the ratio of the absorption coefficients was taken as unity for the purpose of calculating transition probabilities. The results obtained for the ratio ϵ_1/ϵ_2 were very near unity for the wave lengths used.

Some explanation is required for the methods of calculation used in the other cases. We showed that there is no such thing as a definite, steady state when monochromatic light is not used. In our case filters were used, giving about 90% monochromatic light. Some allowance has to be made for the effect of the other 10%, and this cannot be calculated accurately. We showed that the effective light transmitted through the potassium chromate filter was 85% of 3130 Å. and 12% of 3020, neglecting the other two components. One centimeter of a 50% mixture of the citra-

TABLE IV

EXTINCTION COEFFICIENTS

Cis- and Trans-cinnamic Acids

Plate	Wave length, Å.	Thickness, cm.	Acid	Concn., mole per liter	$\log \frac{J_0}{J}$	ϵ	$\frac{\epsilon\ cis}{\epsilon\ trans}$
13	3130	8.98	*cis*	0.0003	0.956	353	0.421*
			trans	.00015	1.136*	844*	
14	3130	2.50	*cis*	.0003	0.284	379	.395
			trans	.00015	.360	960	
16	3130	5.90	*cis*	.0003	.659	372	.382
			trans	.00015	.862	974	
19	3130	9.00	*cis*	.00024	.737	341	.395*
			trans	.00015	1.166*	864*	
18	3020	2.96	*cis*	.0003	0.932	1050	.242
			trans	.00006	.769	4330	
17	3020	1.62	*cis*	.0003	.543	1115	.206
			trans	.00015	1.32	5420	
14	3020	2.50	*cis*	.0003	0.828	1104	.207*
			trans	.00015	2*	5340*	
15	2536	8.69	*cis*	.000006	0.564	10860	.832
			trans	.000006	.678	13050	
13	2536	8.98	*cis*	.000006	.572	10620	.841
			trans	.000006	.680	12620	
15	2650	8.69	*cis*	.000006	.445	8580	.454
			trans	.000006	.980	18870	
13	2650	8.98	*cis*	.000006	.438	8130	.460
			trans	.000006	.952	17660	

The accompanying values of the ratio were taken as averages

Wave length	$\frac{\epsilon\ cis}{\epsilon\ trans}$
3130	0.39
3020	.22
2650	.45
2536	.83

conic and mesaconic solutions used will absorb 2.5% of the 3130 light and 4.1% of the 3020. The relative amounts of light actually absorbed are obtained by multiplying these by the relative strengths of the two lines above. These relative amounts come out to 3.5 and 1, respectively. The ratios of the extinction coefficients ϵ_1/ϵ_2 were 0.22 for 3020 and 0.29 for 3130. The effective value will be somewhere between these two, and for a reasonable mean we take

$$\frac{\epsilon_1}{\epsilon_2} = \frac{3.5 \times 0.29 + 1 \times 0.22}{4.5} = 0.27$$

A similar method was used for calculating a mean value of ϵ_1/ϵ_2 for cinnamic acids, only in this case it was sufficient to assume that absorption was complete. The relative strengths of the two lines concerned are therefore used directly.

Thus, for the potassium chromate filter

$$\frac{\epsilon_1}{\epsilon_2} = \frac{85 \times 0.39 + 12 \times 0.22}{97} = 0.36$$

and for the chlorine filter

$$\frac{\epsilon_1}{\epsilon_2} = \frac{92 \times 0.837 + 8 \times 0.457}{100} = 0.807$$

The photostationary compositions and the probability ratios are summarized in Tables V, VI and VII, and are plotted in Figs. 4 and 5.

TABLE V

PHOTOSTATIONARY CONCENTRATIONS OF MALEIC AND FUMARIC ACIDS

Unfiltered Radiation

Temp., °C.	Percentage maleic	Percentage fumaric	$\frac{\text{Maleic}}{\text{Fumaric}}$	$\frac{9}{1 - p}$
0	71.4	28.6	2.49	2.49
10	71.4	28.6	2.49	2.49
30	69.3	30.7	2.26	2.26
60	69.3	30.7	2.26	2.26
90	69.6	30.4	2.29	2.29

TABLE VI

PHOTOSTATIONARY CONCENTRATIONS OF CITRACONIC AND MESACONIC ACIDS

Potassium Chromate Filter

Temp., °C.	Percentage citraconic	Percentage mesaconic	$\frac{\text{Citraconic}}{\text{Mesaconic}}$	$\frac{p}{1 - p}$
0	69	31	2.2	0.59
25	53	47	1.1	.30
50	48	52	0.92	.25
90	46	54	.85	.23

TABLE VII

PHOTOSTATIONARY CONCENTRATIONS OF *Cis*- AND *Trans*-CINNAMIC ACIDS

Potassium Chromate Filter

Temp., °C.	Percentage *cis*	Percentage *trans*	$\frac{\textit{cis}}{\textit{trans}}$	$\frac{p}{1 - p}$
15	77.0	23.0	3.55	1.21
50	77.3	22.7	3.40	1.22
90	77.1	22.9	3.37	1.21
		Chlorine Filter		
15	54.2	45.8	1.18	0.95
50	54.2	45.8	1.18	.95
70	57.0	43.0	1.33	1.07
80	60.0	40.0	1.50	1.21
90	64.0	36.0	1.77	1.43

Some quantum efficiencies from the results of Warburg[3] and Vaidya[4] are given in Table VIII. Some of the values of $p/(1 - p)$ in the last column are calculated by comparing results from solutions of different concentrations and are not strictly valid.

The Energy Changes Involved in **Isomerization.**—The energy change involved in the isomerization of an acid in dilute solution may be calculated from the heats of combustion and heats of solution. Not only do differences between four quantities, two of them large, come in so that the final result may easily be in error by as much as 1000 calories, but the hydration

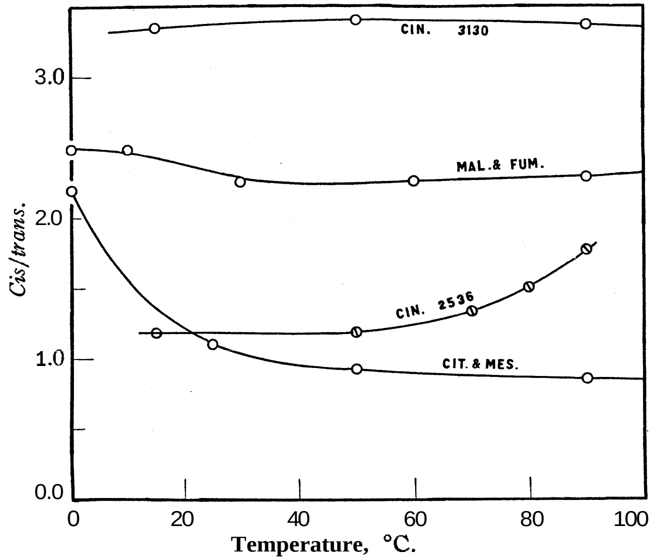

Fig. 4.

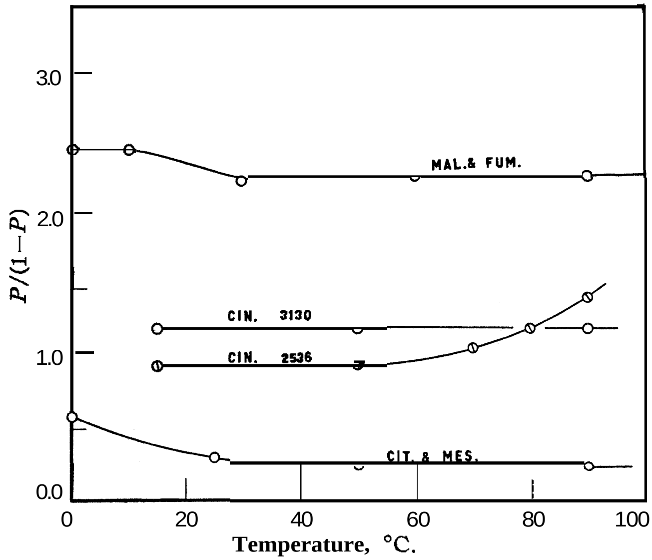

Fig. 5.

TABLE VIII

QUANTUM EFFICIENCIES FROM OTHER SOURCES

Wave length	Concn of acid. (cis) maleic *m*	γ_1	Concn. of acid, (trans) fumaric *m*	γ_2	$p/(1-p)$ = 72/71	Author
2070	0.0102	0.0314	0.0102	0.102	3.25	W.
	.00514	.0358	.00306	.0764	2.14	W.
2530	.0102	.0414	.0102	.0961	2.32	W.
	.00514	.0462	.00306	.0829	1.80	W.
2820	.0102	.0297	.0102	.1291	4.35	W.
	.00514	.0308	.00306	.0983	3.06	W.
3130	.010	.048	.01	.118	2.46	V.
	.005	.0525	.005	.083	1.58	V.
				Mean value	2.62	
	Cis-cin.		*Tr.*-cin.			
3130	0.003	0.206	0.003	0.61	2.96	V.

energies may be changed on activation so that in the citraconic–mesaconic case we do not know which isomer is the more stable. Thus Δ*H* in solution for the reaction cis ⟶ *trans* is —400 cal. for this case. For maleic ⟶ fumaric acid it is about —5000 cal.

Another datum of interest is the activation energy of maleic acid which Höjendahl[16] gives as 15,800 calories. This value was obtained from the rate of thermal isomerization, and was checked by the absorption spectrum of molten maleic acid. This will give us some idea of the order of magnitude of activation energy to be expected in solution.

TABLE IX

THERMOCHEMICAL DATA (CALORIES)

	Heats of combustion for acid = $CO_2 + H_2O$			Mean heats of isomerization (solids) *AH* for *cis* ⟶ *trans*	Heats of solution *AH* for acid = acid (aq.)	Heats of isomerization (solution) *AH* for cis ⟶ trans
Source	Beilstein	Beilstein			I. C. T.	
Author	Luginin	Stohman and Kleber			Gal and Werner	
	Δ*E*	Δ*E*	Δ*H*			
Citraconic	—483,522	—480,000	—479,700		+2800	
Mesaconic	—479,100	—477,500	—477,200		+5500	
Diff.	— 4,422	— 2,500	— 2,500	—3100	—2700	— 400
	AH	*AH*				
Maleic	—327,480	—326,300			+4444	
Fumaric	—319,278	—320,100			+5906	
Diff.	— 6,202	— 6,200		—6200	—1462	—4738
C.-cinnamic			—1,047,000			
T.-cinnamic			—1,041,000			
Diff.			— 6,000	—6000		

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[16] Höjendahl, *J. physik. Chem.*, **28**, 758 (1924).

Discussion

A stationary state with aqueous solutions of mesaconic and citraconic acids has not been reported previously. Stoermer[1] and Vaidya[4] each report no change, but Vaidya seems to have assumed that Stoermer's result for alcoholic solutions would apply to aqueous ones, since he does not describe any experiment to confirm this.

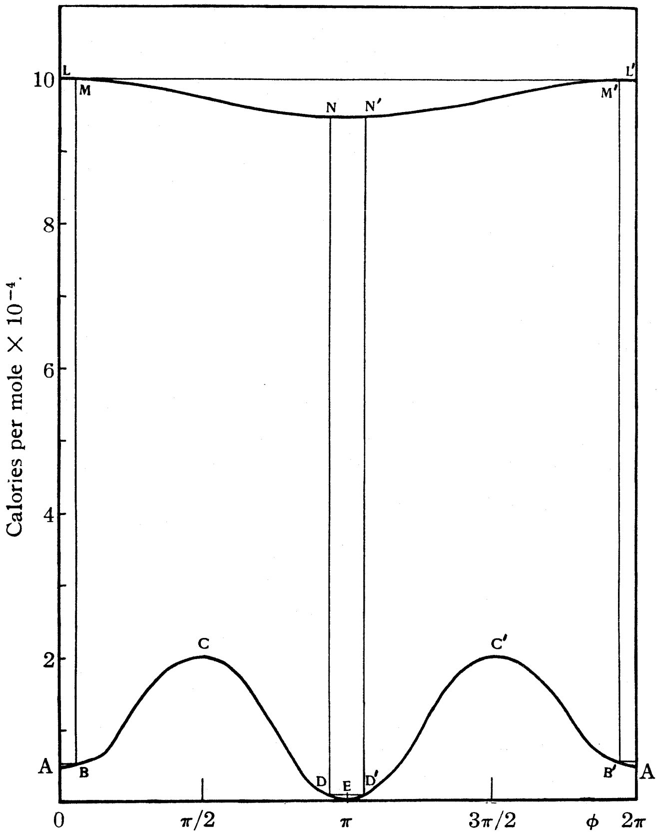

Fig. 6.

The absorption of a quantum of light of wave length 300 will produce an activation of about 95,000 calories per mole. If we assume from Höjendahl's result for the activation energy of maleic acid that 16,000 calories above the normal cis state gives the height of the potential energy humps for unactivated acids, then our energy diagram will be like that in Fig. 6. The upper state will be some sort of potential energy curve a long way above the maxima for the lower curve.

We can now discuss possible shapes for this upper curve. At 300°K., the energy per degree of freedom per mole is $^1/_2$ RT, or about 300 calories.

Thus, an average *trans* molecule will be oscillating along DD' and a cis molecule along B'B in the normal state. When they first reach the upper state, they will therefore be oscillating along NN' and MM', respectively.

Now consider the type of curve in Fig. 7 (i). This is the $V = A - k_1\sin^2\varphi/2$ type, described in the introduction. For cinnamic and fumaric and maleic acids, we may expect AA' to be about 5000 calories above E. The activated cis and *trans* molecules will be oscillating along BB' and DD'. The point of temperature equilibrium is only 600 calories above E, very near to DD'; therefore, no activated *trans* molecules at all will be expected to oscillate above CC', which will be necessary if any cis is to be formed. This potential curve, then, will not fit in with any of the results.

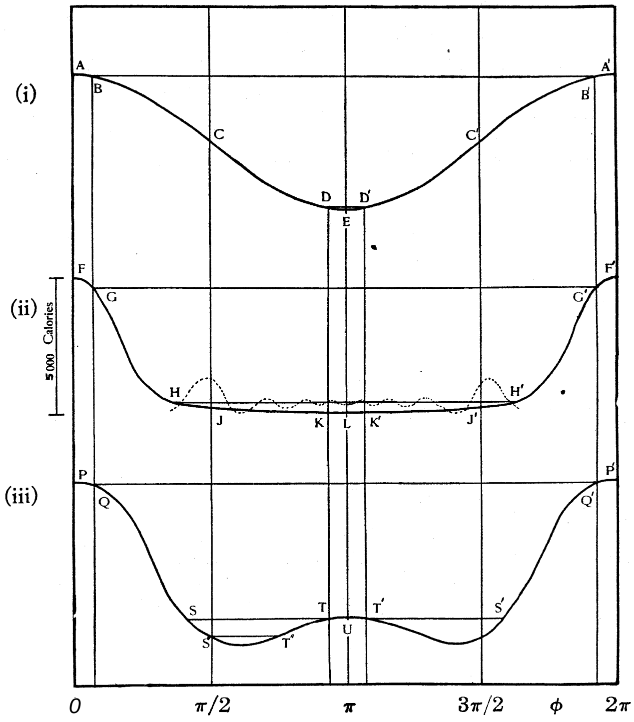

Fig. 7.

Now consider Fig. 7 (ii). On acquiring temperature equilibrium, a molecule will oscillate along HH'. We cannot calculate the ψ function exactly for such a level; all we know from the Schroedinger equation is that

$$\frac{1}{\psi}\frac{\partial^2\psi}{\partial\varphi^2} = -\frac{8\pi^2 I}{h^2}(E - V)$$

Thus, when (E − V) is small, *i. e.*, at H and H', either ψ is large, or its curvature is small. A probable type of curve for \$ is dotted in. Thus, with a potential curve of this sort, any ratio of cis to trans may be produced.

depending on the position of HH' and the steepness of the potential curve. A potential curve of this sort would be expected if the repulsion of the larger groups falls off very rapidly with distance, and if the hydrogen and carboxyl groups (hydrogen and phenyl also in the case of cinnamic acid) exercise no repulsive effect on each other.

If these groups do have steric effects on each other, we shall have a curve of the type in Fig. 7 (iii). There will be two minima, corresponding to configurations which are mirror images, somewhere between the *cis* and *trans* positions. An activated *trans* molecule will vibrate along ST or S'T'. Thus, it will be possible for it to change over to *cis* without coming to thermal equilibrium at all.

An activated *cis* molecule, vibrating along QQ', will have very little chance of becoming a *trans* molecule on deactivation, unless it loses thermal energy, and vibrates along some path S″T″. It would do this after a very few collisions, for its energy is so much higher than the average. With this energy curve, then, we may expect any distribution of the two acids, depending on the magnitude of the subsidiary maximum and the positions of the two minima. There does not, then, appear to be much to choose between (ii) and (iii) except that in (ii) we shall require a longer life in the activated state, so that the *trans* molecule may acquire thermal equilibrium. In the case of fumaric and maleic acids, the quantum efficiencies are low, *i. e.*, most molecules return to their original states on deactivation. This suggests that the time of activation is so short that the activated molecules may not have time to reach thermal equilibrium.[17]

BERKELEY, CALIFORNIA RECEIVED OCTOBER 17, 1932
PUBLISHED APRIL 6, 1933

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(17) Just before this article was submitted for publication, my attention was called to a paper by Mulliken [*Phys. Rev.*, 41, 751 (1932)], in which he concludes that Fig. 7 (iii) represents the potential function for the excited molecule. However, he states that I did not consider this possibility in my earlier paper. In that paper I wrote "nor have we been concerned with the more complicated potential functions for the possible motion which we have discussed. Such departures from simple functions doubtless do occur even for the simplest molecules." I wished merely to postpone such considerations until enough experimental data were available to make such a discussion profitable.—A. R. OLSON.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

The Dependence of Crystallization Velocity on Molecular Structure[1]

BY MAURICE E. KRAHL[2]

Introduction

In discussing the formation of an ordered array of molecules, such as a crystal lattice, from a chaotic phase, such as a liquid or gas, one has to consider not only the mass and velocity of the components of the chaotic phase but their shape as well. Up to the present time there has been very little known about the influence of molecular structure or shape on crystallization. The experiments described in this paper were undertaken in the hope of obtaining some information along these lines. They deal with linear crystallization velocity, which is the rate at which an interface between the solid and liquid phases proceeds along a tube filled with the melted substance.

Because of the essentially planar structure of benzene and its simple derivatives[3] and the increased ease of interpretation of results, several series of di- and trisubstituted benzenes were chosen for study. In addition, a few phenylated hydrocarbons and substituted naphthalenes were measured in order to ensure generality.

Experimental

I. Purification of Materials

In most cases the most convenient and efficient method of purification was recrystallization. Depending on the condition of the original samples, four to seven recrystallizations were made. The purified samples were then dried for a minimum period of a week in vacuum desiccators, evacuated with a Cenco pump.

A few compounds were distilled at reduced pressure through a still with a two and a half foot column, a middle cut being taken from the flat boiling fraction.

II. Apparatus and Method

Glass capillaries, obtained from the Corning Glass Company, served as crystallization tubes. The approximate dimensions of these were: length, 75 cm.; inside diameter, 1 to 2 mm.; wall thickness, 0.3 to 0.5 mm. The capillaries were cleaned by keeping in chromic acid for several days, then washing with water and ethyl alcohol. They were dried by heating evenly with a small gas flame while a current of nitrogen, previously dried by sulfuric acid (sp. gr. 1.84), was passed through them for fifteen minutes.

The small test-tubes for melting were cleaned with chromic acid, water and alcohol, plugged with cotton and dried in an oven at 110° for three hours.

The observation tube was made of Pyrex glass tubing, 2 cm. in diameter and 65 cm. long. By means of two side arms it was connected through small copper tubing, well insulated with asbestos, to a small rotary pump and the reservoirs for the bath

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(1) From the Dissertation of Maurice E. Krahl submitted to the Board of University Studies of The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1932.

(2) Eli Lilly and Co, Fellow in Chemistry.

(3) Wierl, Ann. *Physik*, **8**, 621 (1931).

liquid. The bath liquid was heated or cooled in the reservoirs to the temperature desired and pumped through the observation tube at a rate of approximately one liter per minute. The temperature was measured by means of a thermometer suspended in the observation tube. At intervals of ten centimeters along this observation tube fine lines were etched with hydrofluoric acid solution. To aid in accuracy of reading, the lines were made in pairs as two opposite segments of a circle around the tube. A total range of 50 cm. was available for the crystallization.

The heating tube, for melting the contents of the filled capillaries, was made from Pyrex glass tubing 1 cm. in diameter and 65 cm. long. This was wound evenly with a nichrome coil of suitable resistance.

A pentane thermometer, range −200 to 50°, was used for all temperatures below 0°. For the higher temperatures three mercury-filled thermometers were used interchangeably. These were checked against a Bureau of Standards thermometer.

Because of the wide range of temperature, it was necessary to have three different bath liquids at various times during the investigation. These were used as follows: below 0°, 95% alcohol; 0 to 75°, water; above 75°, a colorless, transparent mineral oil sold commercially as "Oilax." The quantity of bath liquid and regulation was such that the maximum temperature fluctuation during the course of a single reading was 0.2° for water, 0.5" with alcohol and 0.5" with oil.

The timing was done with two Meylan stop watches. One was checked by the Meylan Watch Company before this investigation; the other was checked against the first.

The procedure in measurement may be described very simply. The material for crystallization was melted in a small test-tube and drawn into the capillary by suction. The ends of the capillary were then sealed off. If the material melted above room temperature, it was necessary to suspend the heating tube directly above the observation tube and to remelt the contents of the filled capillary, leaving a small amount of solid in the bottom for seeding. The capillary was then dropped into the observation tube, and, as the crystallization occurred from the seed at the bottom, a record was made of the time required for the solid–liquid interface to proceed between any two marks on the observation tube. Preliminary measurements showed that the direction of the growth up or down the tube did not affect the rate.

In measuring compounds with comparatively low rates, it was found by making duplicate successive determinations with two watches that a constant rate was reached by the time the growth interface was opposite the lowest mark on the observation tube. In more rapid crystallizations a constant rate was attained only after the growth had proceeded to a mark 10 or even 20 cm. from the bottom of the capillary. This point was determined for each individual substance and subsequent measurements made accordingly.

III. Data and Results

Preliminary Experiments.—A series of fifty-one observations with nine different capillary tubes, varying in outside diameter from one to two millimeters, showed that capillary size, number of remeltings, temperature of melting and time of aging did not affect the crystallization velocity of benzophenone by more than the experimental error of one per cent. It was essential that this be known to ensure reproducibility of later measurements.

Temperature Dependence of the Crystallization Velocity.—The actual form of the curve obtained when the crystallization velocity is plotted against supercooling is shown in Fig. 1, which gives the experimental results for m-dihydroxybenzene. The particular curve given here is typical of the curves for the other substances whose maximum velocities are given in Tables I and II.

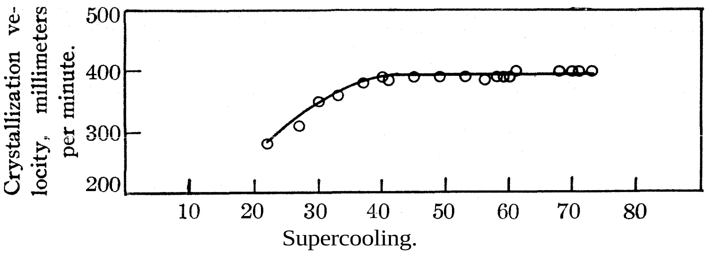

Fig. 1.

Linear Crystallization Velocities of Some Substituted Benzenes and Phenyl Substituted Hydrocarbons.—The experimentally determined velocities for a few simple di- and trisubstituted benzenes, and for some phenyl substituted methanes, ethanes and ethylenes are given in Table I.

TABLE I

Compound	M. p., °C.	ΔT	Maximum velocity, meters per minute
o-Dichlorobenzene	−17.6	19–36	2.2
m-Dichlorobenzene	−24.8	21–28	0.70
p-Dichlorobenzene	52.9	20–35	25
p-Dibromobenzene	87.3	27–54	7.5
1,2,4-Trichlorobenzene	17.0	25	0.025
1,3,5-Trichlorobenzene	63.4	25–33	7
1,3,5-Tribromobenzene	119.6	29–52	2.4
o-Dihydroxybenzene	104.0	29–59	1.7
m-Dihydroxybenzene	116.0	37–74	0.40
p-Dihydroxybenzene	169.0	35–47	6.3
o-Diaminobenzene	103.8	41–56	7
p-Diaminobenzene	140.0	37–47	10
m-Dinitrobenzene	89.7	49–59	6
p-Dinitrobenzene	172.1	41–50	15
o-Bromobenzoic acid	148.0	32	0.80
m-Bromobenzoic acid	153.0	14	0.255
m-Bromoaniline	18.5	22–63	0.048
p-Bromoaniline	66.4	43	1.6
Diphenyl	69.0	16	7.5
Diphenylmethane	25.2	23–27	0.53
Triphenylmethane	93.1	25–30	0.027
1,2-Diphenylethylene	123.9	25–37	2
1,1-Diphenylethylene	8.2	21–25	0.016
1,2-Diphenylethane	50.8	30–36	0.70
1,1-Diphenylethane	−25.9	27–40	Less than 0.001
1,1,1-Triphenylethane	94.3	39	0.08
1,1,2-Triphenylethane	48.0	28	Less than 0.001

The number of significant figures in the values of the velocities is that justified by the accuracy of the measurement. A T is the range of supercooling, expressed in degrees below the melting point, in which the maximum velocity was maintained. The width of this region varies because at great supercooling the rate of spontaneous nuclei formation became too great to permit linear velocity measurements. In cases where this prevented a constant maximum being reached, only one temperature is given.

Linear Crystallization Velocities of Some Substituted Naphthalenes.—The number of substituted naphthalenes which can be measured is limited by two factors, the high melting points and the difficulty of purification of such compounds. Results with a few of the most usable compounds are given in Table II.

TABLE II

Compound	M. p., "2.	A T	Maximum velocity, merers per minute
a-Naphthol	96.0	44	0.275
β-Naphthol	122.0	53	6
α-Chloronaphthalene	–26.1	27–38	0.029
a-Iodonaphthalene	4.2	11–16	.001
β-Iodonaphthalene	54.0	7	.30

The values for β-chloronaphthalene, which have not been included, and for β-iodonaphthalene are of doubtful value because of the extremely short range of supercooling which was permitted by the rapid spontaneous nuclei formation.

Discussion and Conclusions

The crystallization velocities given in Tables I and II are additions to and corrections of those previously reported.[4]

Since the dependence of the crystallization velocity on temperature has been discussed by Tammann,[5] no further mention of it need be made here.

From Tables I and II the generality of the effect of molecular structure on crystallization rates is apparent. Of the isomeric disubstituted benzenes, the order of decreasing velocity in each series is para, ortho, meta. For the trisubstituted chlorobenzenes the symmetrical 1,3,5 isomer has a much greater velocity than the 1,2,4. Similarly, the 1,2 disubstituted ethylenes and ethanes crystallize much faster than the less symmetrical 1,1 isomers. From the evidence thus far available, it appears that the β-mono substituted naphthalenes crystallize faster than the isomeric α-compounds.

It appears from these experimental results that there exists a relationship between crystallization velocity and molecular symmetry. Before this relationship can be made a definite one, all of the properties of the liquid and crystal states which influence crystallization velocity must be considered.

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(4) Krahl, THIS JOURNAL, 54, 1256 (1932).

(5) Tammann. "Aggregatzustände," Leipzig, 1922. pp. 247–272.

By taking account of the probable form of the molecules, as well as the properties referred to above, an explanation has been found for the variations in velocity which are shown experimentally. In order that this explanation may be shown to be valid for all crystallization processes, whether from liquid or vapor, it is necessary to have further experimental evidence concerning the structure of the molecules of the substances whose crystallization velocities have been measured. To this end, x-ray investigations of interatomic distances are now being carried out in this Laboratory for a number of compounds in the gaseous state. As soon as this final point has been definitely established, the explanation referred to above for the effect of molecular symmetry on crystallization rates will be published.

The author wishes to thank Professor D. H. Andrews for his helpful advice and criticism during the course of this work. He is also indebted to Dr. Emil Ott for much valuable advice in respect to the conclusions to be drawn from the experiments. He wishes also to acknowledge his indebtedness to Eli Lilly and Company for a fellowship granted to him under the State Fellowship Plan.

Summary

1. The linear velocities of crystallization have been measured for thirty-four compounds of related molecular structure. The results bear out the hypothesis that, of a series of isomers, the most symmetrical compound crystallizes fastest.

2. It has been shown that the temperature and time of melting, the number of remeltings and the time of aging of the melt do not affect the crystallization rate.

BALTIMORE, MARYLAND

RECEIVED OCTOBER 18, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM LEIGHTON HALL OF CHEMISTRY, CARLETON COLLEGE, AND FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 342]

The Crystal Structure of Ortho-Iodobenzoic Acid

BY HAROLD P. KLUG

x-Ray analysis of organic crystals usually leads no farther than to the determination of a possible unit cell and the space group. Occasionally it is possible to probe a bit more deeply into the arrangement in the cell. In these cases the results are of interest for stereochemical considerations of the molecule and the molecular arrangement within the cell. It seems worth while at this time to report the results of the study of o-iodobenzoic acid, which has led to the determination of the positions of the iodine atoms in the cell.

Groth[1] gives the following data for this monoclinic crystal: $a:b:c = 0.7964:1:0.2880$, $\beta = 110° 25.5'$; m. p. 161°; sp. gr. 2.249. The material used in this investigation was Eastman Kodak Company chemically pure product further purified by two vacuum sublimations. The resulting product was colorless and melted at 161.6–162.0°. The crystals used were grown from ether or from a mixture of equal parts of ethyl and isoamyl acetates. These were needles along the c axis with the prism faces (110) developed. Small end faces (011) and (101) were also present. The structure analysis was made by means of powder, Laue and oscillation photographs.

The Unit of Structure.—Powder photographs[2] were taken with Mo K_α radiation, using sodium chloride as a standard. These were analyzed by the usual methods, and required a 4-molecule cell to account for all the lines.

Laue photographs[2] were taken with the incident beam of x-rays nearly perpendicular to (010), (110), and inclined at an angle of approximately 20° to the normal to (110). The short wave length limit of the incident beam (from a tungsten target) was 0.31 Å. The assumption of a 4-molecule cell gave $n\lambda$ values down to 0.31 Å. but not below. As in the case of *m*-iodobenzoic acid,[3] the strongly absorbing iodine absorbed all wave lengths between its critical absorption limit 0.37 If., and the short wave length limit, 0.31 Å., except in the case of a very few spots. Thus most of the first-order spots had an $n\lambda$ value between 0.37 If. and 0.48 Å.

Oscillation photographs were taken with Mo K_α radiation using a cylindrical film, the crystal being oscillated through 15° about a crystallographic axis in each case. These were indexed by Bernal's graphic method,[4] and the fundamental translations of the unit cell were calculated by the

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(1) Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. IV, p. 465.

(2) These photographs were taken at Ohio State University, Columbus, Ohio, in 1926–1927 while the author was a graduate student there.

(3) Klug, Mack and Blake, Tars JOURNAL, **51**, 2882 (1929).

(4) Bernal, Proc. Roy. *Soc.* (London), **A113**, 117 (1927).

Polanyi formula from careful measurements of the layer lines. The dimensions of the unit cell are

$$a_0 = 11.71 \text{ Å}. \quad b_0 = 15.17 \text{ Å}. \quad c_0 = 4.336 \text{ Å}. \quad \beta = 110° \, 28.5'$$

The axial ratios calculated from these data are $a:b:c = 0.7719:1.0.2863$, in good agreement with the crystallographer's values above.

The Laue photograph with the incident beam perpendicular to (010) showed two pseudo planes of symmetry almost at right angles to each other. Because of this pseudo-orthorhombic nature a more desirable cell can be formed by making the short diagonal of the projection of (010), based on Groth's axial ratios, the (001) of a new cell. The dimensions of the new 4-molecule cell are (calculated from x-ray data)

$$a_0 = 11.30 \text{ Å}. \quad b_0 = 15.17 \text{ Å}. \quad c_0 = 4.336 \text{ Å}. \quad \beta = 90° \, 43' \, 47''$$

These lead to the new axial ratios $a:b:c = 0.7450:1:0.2863$ with $\beta = 90°$ 43' 47". Oscillation photograph No. 5 about Groth's *a* axis confirmed the desirability of the new choice of cell. It is also in keeping with the crystallographic custom of choosing the axes so as to make angle β as nearly 90° as possible. The end faces on the crystal designated (101) and (011) by Groth now become (001) and ($\bar{1}11$), respectively, with the new set of axes. All photographs were analyzed on the basis of the new axes, and all indices in this paper refer to the cell based on these axes.

The Space Group.—The space group determination was based on the data from the Laue photographs. Since first-order Laue reflections were observed from all types of pyramidal planes the space group is based on the simple monoclinic lattice Γ_m. All types of prism planes were found to be present in the first-order (Table I) except ($h0l$) when h is odd, and ($0kl$) when k is odd. The latter has no significance from a space group standpoint in the monoclinic system, but indicates a pseudo-glide plane parallel to (100) with a translation of $b/2$. Actually the reflections (011), (031) and

TABLE I

FIRST-ORDER PRISM REFLECTIONS ON LAUE PHOTOGRAPHS

Photograph No. 2				Photograph No. 3			
Planes reflecting		Planes not reflecting		Planes reflecting		Planes not reflecting	
(hkl)	$n\lambda$	(hkl)	$n\lambda$	(hkl)	$n\lambda$	(hkl)	$n\lambda$
405	0.45	$10\bar{2}$	0.46	$20\bar{3}$	0.55[a]	504	0.39
$20\bar{3}$	.44	103	.40	403	.55[a]	704	.49
023	.43	304	.53[a]	$06\bar{5}$	.52[a]	$50\bar{4}$	.58[a]
$04\bar{3}$	.46	$30\bar{4}$	.37	$4\bar{3}0$	.48	$30\bar{4}$	.44
$\bar{7}90$	.39	305	.37	$7\bar{5}0$	.34	$70\bar{5}$	.48
$\bar{5}70$	.39	506	.39	850	.44	$70\bar{6}$	.38
$\bar{3}70$	.42			$\bar{5}60$	.41		
$\bar{9}.10.0$	.46			$17.\bar{7}.0$	.38		
4.11.0	.44			$17.\bar{5}.0$	.48		
$\bar{5}.16.0$	.40						

[a] The short wave length limit in the case of these photographs was known to be at 0.31 Å.

(032) were observed on oscillation photographs, showing that the approximation to an arrangement requiring $(0kl)$ absent when k is odd, while close, is not complete. Since all of the $(h0l)$ planes with h odd listed in Table I were in a position to reflect in the first order on some one of the Laue photographs, but failed to, their absence has been assumed to be a legitimate space group absence.

One other absence occurs on oscillation photograph No. 2. All odd orders of $(0k0)$ are absent, while (020), (040), (060) and (080) are present. The only monoclinic space group requiring the observed absences is C_{2h}^5 which, therefore, has been accepted as the correct one. All data from the various types of photographs are in agreement with this choice.

Atomic and Molecular Arrangement in the Cell.—For small orders of reflection in the case of a compound like o-iodobenzoic acid, the benzene rings no doubt contribute very little to the intensities because of their large self-interference. Thus the intensities observed are due largely to the scattering of the heavy iodine atoms which make up more than half the weight of the molecules. By neglecting the carbon, hydrogen and oxygen atoms, and assuming the intensities to be due entirely to the iodine atoms, it is possible to locate the positions of the iodine atoms reasonably accurately.

In space group C_{2h}^5 the four iodine atoms could all be equivalent, or they might be divided into two sets of two equivalent atoms. The latter case places the iodine atoms in centers of symmetry. The observation on oscillation photograph No. 3 of $(400) > (200)$ rules this out. It is also chemically improbable that the iodine atoms would occupy these centers of symmetry. The iodine atoms are located, therefore, in the four general positions. Wyckoff's[5] coordinates for these positions (interchanging his b and c indices to make the coordinates agree with the choice of axes used in this paper) are

$$xyz;\ \tfrac{1}{2} - x, y + \tfrac{1}{2}, \bar{z};\ x + \tfrac{1}{2}, \tfrac{1}{2} - y, z;\ \bar{x}\bar{y}\bar{z}$$

The oscillation photographs furnish data for evaluating these parameters with fair accuracy.

In this case, neglecting extinction, a quantity proportional to the integrated intensity of reflection of the Mo K_α line from a plane (hkl) is S^2, where

$$S = \left(\frac{1 + \cos^2 2\Theta}{2 \sin 2\Theta}\right)^{1/2} \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

in which f_n is the usual atomic scattering factor for the **n**th atom. The f value for iodine used in this paper was obtained from Pauling and Sherman's recent paper.[6] Approximate values for each of the parameters were determined from the appropriate set of pinacoid reflections by cal-

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(5) Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institution Publication No. 318. Washington. 1922, p. 51.

(6) Pauling and Sherman, Z. *Krist.*, 81, 27 (1932).

culating $\mathbf{S}^2$ values and comparing them with the observed intensities visually estimated. The curves in Fig. 1 show that the observed intensities, (400) > (200) > (600) > (800), (060) > (020)≅(040) > (080), and (001) > (002) > (003), are approximately satisfied by the following

$x = 0.10, 0.15, 0.35$ or 0.40
$y = 0.09, 0.16, 0.34$ or 0.41
$z = 0.00 \pm 0.05$ or 0.50 ± 0.05

The various combinations of the above parameters narrow down to four lion-identical cases to be considered:

1. $x = 0.10$ $y = 0.09$ $z = 0.00 \pm 0.05$
2. $x = 0.10$ $y = 0.16$ $z = 0.00 \pm 0.05$
3. $x = 0.15$ $y = 0.09$ $z = 0.00 \pm 0.05$
4. $x = 0.15$ $y = 0.16$ $z = 0.00 \pm 0.05$

To determine the correct set of x and y parameters, values of $\mathbf{S}^2$ for a set of $(hk0)$ planes were calculated for the four combinations above, and for small deviations from the values listed in the combinations, and compared with the observed intensities (Table II). The best values were found to be $x = 0.14$ and $y = 0.08$. The value for z was found to be close

TABLE II

INTENSITY DATA FROM PINACOID AND PRISM REFLECTIONS ON OSCILLATION PHOTOGRAPHS

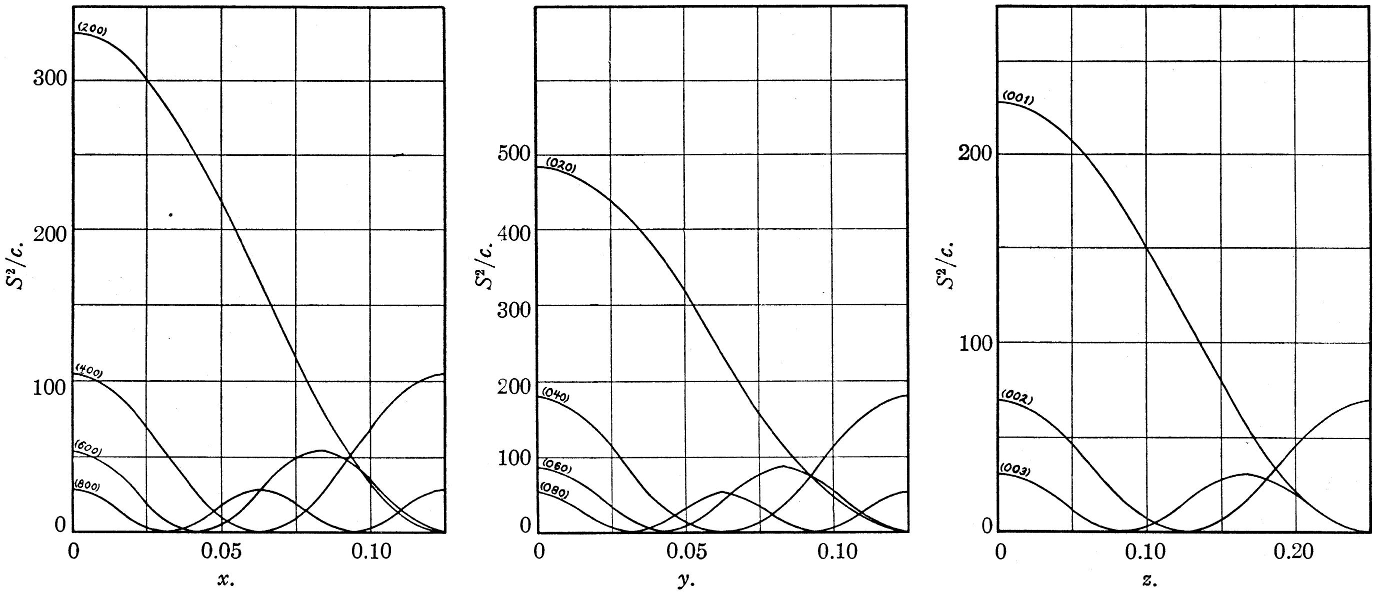
(S^2 based on the final parameter values; $x = 0.14$, $y = 0.08$ and $z = 0.02$)

Pinacoid Reflections

Photograph No. 2			Photograph No. 3			Photograph No. 4		
(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/15000$
020	6	11.0	200	5	5	001	6	13
040	6	3.0	400	8	20	002	4	4
060	8	8.5	600	4	6	003	2	2
080	3	2 0	800	2	2			

Prism Reflections

A. $(hk0)$ Photo. No. 3			B. $(0kl)$ Photo. No. 4			C. $(h0l)$ Photo. No. 3		
(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$
310	8	19.8	011	5	0.2	$\bar{2}01$	2	0.1
420	5	4.6	021	9	10.2	$\bar{4}01$	7	14.7
510	1	1.0	022	3	3.5	$\bar{6}01$	3	1.6
520	5	8.8	023	4	1.6	$\bar{8}01$	1	3.4
620	1	0.8	031	$^1/_2$	0.4	201	7	3.0
630	5	6.6	032	$^1/_{10}$	0.7	401	7	12.2
720	1	0.1	041	2	3.8	601	5	3.7
730	1	.03	042	6	1.8	801	2	2.1
740	1	.1						
750	1	3.7						
830	2	2.4						
840	1	0.5						
850	2	.7						
860	2	2 2						
940	1	3 0						



Crystal structure of ortho-iodobenzoic acid. Crystal structure of ortho-iodobenzoic acid. Crystal structure of ortho-iodobenzoic acid.

Fig. 1.—Structure factor curves for the various pinacoid reflections for ranges of values of the parameters leading to non-identical structures.

to 0.02 by calculating values of S^2 for sets of $(h0l)$ and $(0kl)$ planes and comparing with observed intensities (Table II).

It must be remembered that complete agreement is not to be expected between the calculated and observed intensities in this analysis, since the effect of the carbon and oxygen atoms has been neglected entirely. Inasmuch as a change of a very few hundredths in the values of the parameters destroys the qualitative agreement, the results may be accepted with considerable faith.

Figure 2-A is a projection on (001) parallel to the c axis. The positions of the iodine atoms are represented by the circles. The closest distance of approach between the two iodine atoms (its projection is indicated on the drawing by 1) was calculated to be 3.99 Å. The next closest approach between two iodine atoms is along the c axis, and is equal to c_0 = 4.34 Å. Both of these values are reasonable and, in fact, are in excellent agreement with the distances found in the organic crystal iodoform. Hendricks[7] has calculated from I. Nitta's work on iodoform[8] that the closest approach of iodine atoms in adjacent molecules is 3.94 Å. and the next closest is 4.43 Å. Huggins and Noble[9] have found almost identical values from their study of iodoform. Thus the agreement is complete within the accuracy of the values of the parameters themselves, which in the case of each crystal is probably about ±0.1 Å.

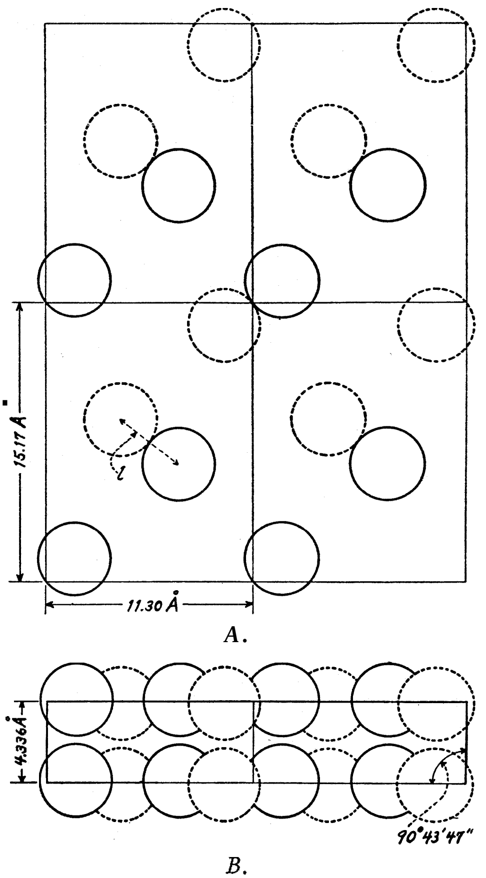


Fig. 2.— (A) Projection of four unit cells on (001) parallel to the c axis. The dotted circles represent iodine atoms at a distance of 0.087 Å. below the (001) plane, and the full circles iodine atoms at the same distance above (001). (B) Projection of two cells on (010).

From Fig. 2-A the two-fold screw axis and the glide plane perpendicular

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(7) Hendricks, *Chem. Reviews*, 436 (1930).

(8) Nitta, *Sci. Papers Inst. Phys.-Chem. Research* (Tokyo), 4, 49 (1926).

(9) Huggins and Noble, *Am. Mineral.*, 16, 519–25 (1931).

to it are evident. Also the pseudo-glide plane parallel to (100) is readily observed. The projection of the cell on (010) (Fig. 2-B) makes evident a pseudo-plane of symmetry parallel to (001). Thus the symmetry and pseudo-symmetry of the observed x-ray reflections are all accounted for by the resulting structure.

It is difficult to make any statement concerning the location of the remainder of the molecule in the cell. The diameter of the plane benzene ring exclusive of the hydrogen atoms is approximately 4.26 Å. Since the hydrogen atoms are believed to be in the plane of the ring of carbon atoms, the plane of the benzene ring cannot be parallel to the c axis. Further location of the remainder of the molecule is not profitable at this time.

The author wishes to express his heartiest thanks to Dr. Linus Pauling for his helpful discussions and valuable advice during the interpretation of the data. The author also wishes to acknowledge with gratitude the financial assistance of Carleton College, which has made possible this research.

Summary

By the use of powder, Laue and oscillation photographs, the crystal structure of ortho-iodobenzoic acid has been investigated. It was found to have a 4-molecule cell with the following dimensions

$$a_0 = 11.30 \text{ Å}. \qquad b_0 = 15.17 \text{ Å}. \qquad c_0 = 4.336 \text{ Å}. \qquad \beta = 90^\circ\, 43'\, 47''$$

The corresponding axial ratios are $a:b:c = 0.7450:1:0.2863$ with $\beta = 90^\circ$ 43'47". The space group is C_{2h}^5. The iodine atoms are in the general positions with the following parameters: $x = 0.14$, $y = 0.08$ and $z = 0.02$. These lead to the closest distances of approach between iodine atoms of adjacent molecules of 3.99 Å. and 4.34 Å., values which are reasonable.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Contribution to the Study of the Hydrogen–Oxygen Reaction. The Adsorption of Hydrogen on Pyrex and Quartz

BY ARTHUR TANDY WILLIAMSON

In a paper[1] which considered the relation of the walls to the initiation of reaction chains in mixtures of hydrogen and oxygen a theory was advanced to explain the upper explosion limit obtaining in such systems. The chief postulate was that the partial pressure of hydrogen in the gas phase was just sufficient to saturate the walls with hydrogen at the critical explosion pressure, and that if the latter were lowered ever so slightly partial desorption would occur. This would be followed by a "flank attack" of the oxygen through the freshly exposed surface, and the sweeping off of the whole surface film as the first step of the explosion.

The purpose of the investigation to be described below was to test this theory by the experimental determination of rates of adsorption and equilibrium measurements for the systems quartz–hydrogen and Pyrex–hydrogen in the temperature range where explosions occur. Earlier workers found that large quantities of hydrogen were taken up by the porcelain[2] and Pyrex[1] above 400°, but the determination of the pressure required to saturate the surface at various temperatures, and of the rates with which the two phases approach equilibrium at constant pressure, remained incomplete. More recently it was shown[3] that hydrogen was adsorbed on silica at 550°, but the figures obtained were sufficient to give only a qualitative idea of the rate of saturation of the surface. However, the same paper contains an analysis of the surface reaction of hydrogen and oxygen which leads the authors to take issue with Alyea's explanation of the upper limit.

The molecular adsorption of hydrogen on quartz[4] is known to be barely measurable at liquid-air temperatures. Diffusion takes place through quartz walls above 300°,[5] and increases exponentially with temperature.[6] Pyrex, in spite of its great adsorbing power, is impermeable[6] to hydrogen, although slight surface reduction takes place.

Apparatus

Cylindrical bulbs of Pyrex and quartz filled with about 90 g. of pulverized Pyrex and quartz, respectively, were cleaned with dilute nitric acid, washed thoroughly with distilled water, and dried by heating and pumping off. They were placed in the brass core of a well-lagged resistance furnace, and sealed onto the system with capillary tubing.

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(1) Alyea, THIS JOURNAL, 53, 1324 (1931).

(2) Bone and Wheeler, *Phil. Trans.*, A206, 1 (1906).

(3) Garstang and Hinshelwood, *Proc. Roy. Soc.* (London), A134, 1 (1931).

(4) Paranjpe, *Proc. Asiatic Soc. Bengal*, 15, 136 (1919).

(6) Johnson and Burt, *J. Opt. Soc. Am.*, 6, 734 (1922).

(6) Williams and Ferguson, THIS JOURNAL. 44, 2160 (1922).

The rest of the system consisted of a compensated gas buret, a closed arm mercury manometer, an electrolytic hydrogen generator with purifying train, and the various pumps The furnace was held at the required temperature by a Leeds and Northrup thermoregulator actuated by a platinum resistance thermometer. The temperature of the packed bulb was read by means of a calibrated chromel–alumel thermocouple which was sunk in an insulated well in the brass core of the furnace and connected to a Type K Leeds and Northrup potentiometer.

Procedure.—The general method of carrying out adsorption measurements has been described frequently.[7] In this particular case the "dead spaces" were determined with helium below 300°, the gas laws being used for extrapolation into the higher temperature range. When the bulbs were first sealed on they were given a pretreatment with hydrogen at 500° for several hours to remove any easily reducible matter. Subsequently, all determinations were preceded by at least twenty-four hours of evacuation, quartz being heated to 600° and Pyrex to 550° during this process.

All values given below have been reduced to standard conditions.

Results with Quartz.—An attempt was made to obtain an isotherm at 565° by admitting successive portions of hydrogen and waiting for the pressure to reach equilibrium. Unfortunately, the rate of diffusion of hydrogen through quartz parallels the rate of adsorption to such an extent that loss of gas by the former process becomes appreciable when the temperature is raised to a point at which adsorption is reasonably rapid. For this reason the isotherm had to be abandoned after two weeks' contact time. Of a total of 19.9 cc. introduced into the bulb only 14.4 cc. could be recovered by evacuation at 600°.

RATE OF ADSORPTION OF HYDROGEN ON QUARTZ

TABLE I

P, 760 Mm. Temp., 400°

Time, min.	$V_{\text{ads.}}$, cc.
0	0.00
2	.15
15	.35
35	.45
80	.50
400	.55
1200	.60
1560	.65
2640	.85

TABLE II

P, 760 Mm. Temp., 446"

Time, min.	$V_{\text{ads.}}$, cc.
0	0.0
1	.2
15	.6
30	.8
45	.9
60	1.1
90	1.3
120	1.4
255	1.5
585	1.7
1515	1.9

TABLE III

P, 760 Mm. Temp., 476"

Time, min.	$V_{\text{ads.}}$, cc.
0	0.0
2	0.4
15	1.1
30	1.3
45	1.5
60	1.7
120	2.0
180	2.1
240	2.2
660	2.6
1320	3.0

RATE OF ADSORPTION OF HYDROGEN ON PYREX

TABLE IV

P, 760 Mm. Temp., 526°

Time, min.	$V_{\text{ads.}}$, cc.	Time, min	$V_{\text{ads.}}$, cc.
0	0.0	30	1.7
5	.4	38	2.2
10	.7	51	2.8
16	1.0	60	3.3
20	1.1	75	3.8
25	1.4		

TABLE V

P, 760 Mm. Temp., 542°

Time, min.	$V_{\text{ads.}}$, cc.	Time, min.	$V_{\text{ads.}}$, cc.
0	0.0	26	3.0
3	0.4	32	3.4
6	0.9	38	4.0
10	1.5	47	4.2
15	2.0	52	4.6
20	2.5	59	4.9

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(7) Pease, THIS JOURNAL, **45**, 1197 (1923); Taylor and Williamson, *ibid.*, **53**, 2168 (1931).

Rate measurements were next carried out under conditions which permitted introduction of the gas at constant pressure, the chosen value being 760 mm.

These rate determinations are shown graphically in Fig. 1. Because of the relatively low temperatures and the short time of contact the gas was almost completely recoverable on evacuation at 600°.

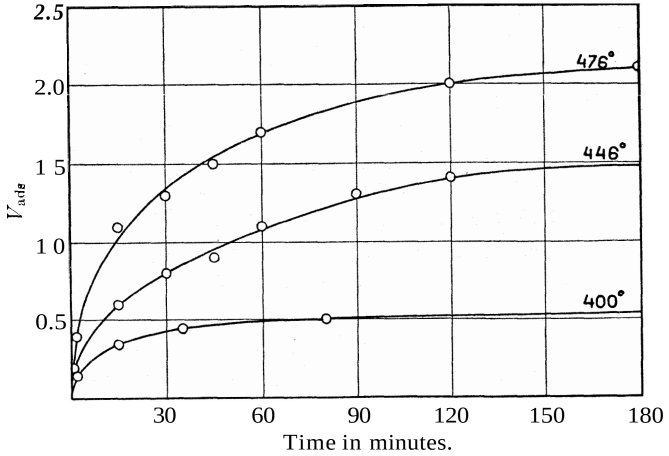

Fig. 1.—Rates of adsorption of hydrogen on quartz.

Results with Pyrex.—The impermeability to hydrogen and the relatively high power of adsorption shown by this glass led to results which were quite conclusive. The rate of adsorption was first determined with the results given in Tables IV and V.

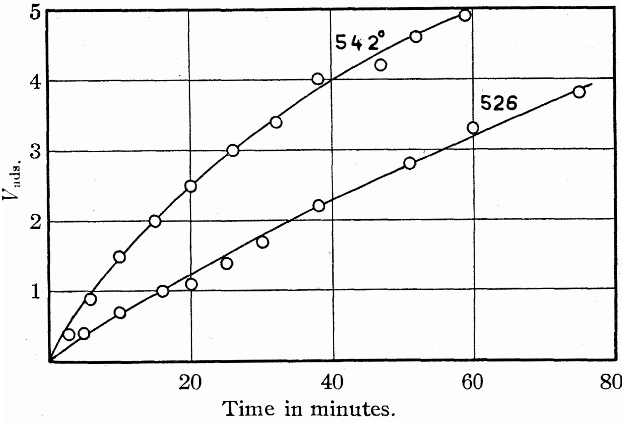

Fig. 2.—Rates of adsorption of hydrogen on Pyrex.

The measurements are plotted in Fig. 2. The gas was almost completely recoverable at 550°, evacuation being continued for thirty-six hours.

Finally, equilibrium values were successfully obtained at 542°, making it possible to construct an isotherm. The values follow.

TABLE VI

ISOTHERMAL ADSORPTION OF HYDROGEN ON PYREX

Temp., 542°

$V_{\text{ads.}}$	P	$P/V_{\text{ads.}}$
0.0	0	..
18.3	181	9.89
16.9	48	2.84
16.2	40	2.47

Gas admitted = 22.5 cc.
Gas recovered = 21.3 cc.

The total time of contact was sixty-two hours, and when this is considered with the recovery efficiency of approximately 95%, it becomes evident that loss of hydrogen by reduction of the Pyrex or by diffusion occurs at a rate which is negligible compared with the velocity of adsorption.

Conclusions.—The rate measurements obtained with quartz show marked acceleration with temperature. In no case, however, is there any evidence of the break which would be expected if fairly rapid adsorption were followed by slow diffusion processes. We may therefore conclude that the formation of a saturated surface layer will only be realized after a relatively long time in this temperature region, and that such a layer when formed will not respond instantly to changes in pressure of the hydrogen in the neighboring gas phase.

Definite corroboration of this view is obtainable with Pyrex. True adsorption will satisfy the Langmuir isotherm

$$\sigma = \frac{bP}{1 + bP} \text{ or } V_{\text{ads.}} = \frac{aP}{1 + bP}$$

where a is the fraction of the available surface which is covered, a and b are constants, P and $V_{\text{ads.}}$ being already defined in this article. The equation may be rearranged to give

$$\frac{P}{V} = \frac{b}{a}P + \frac{1}{a}$$

If we plot the function P/V against P, points on a true adsorption isotherm should therefore give a straight line whose slope is b/a and whose intercept on the ordinate is $1/a$. This procedure has been adopted for the values from Table VI.

The non-horizontal straight line so obtained shows clearly that the preponderating process is true adsorption and not some form of solution. If the latter were the case the results would obey Henry's law and the slope of the curve would be zero. Having obtained a linear relation for the experimental points extrapolation is made easy, and we can link the adsorption measurements with values obtained in kinetic studies.

Unpublished results of Frost in Princeton have shown that the upper explosion limit of a $2H_2O:O_2$ mixture in contact with Pyrex at 542° is approximately 120 mm. total, which means a hydrogen partial pressure of 80 mm. Inspection of the curve drawn from Table VI shows that this corresponds to a P/V value of 4.55 which in turn yields 17.6 cc. as the quantity adsorbed at equilibrium. If now we turn to Table V, it will be found that exposure of the system to hydrogen at a pressure of one atmosphere for an hour will result in the adsorption of only 5 cc. The attainment of the equilibrium value would require an exposure of several hours at one atmosphere, and would require a somewhat longer time if the pressure were markedly lower. Furthermore, the rate of adsorption has been shown to decrease rapidly as the temperature is lowered, the decrement shown in Fig. 2 being roughly 50% for a sixteen degree drop. This means that surface saturation in the neighborhood of 450° will be a process requiring several days.

On the other hand, several investigators have found that the upper explosion limit is a reproducible quantity which can be obtained within a few seconds of the introduction of the gas mixture, in spite of the fact that only a tiny fraction of the surface can be covered in this time. Explosions can still be obtained at 450°, and it has been shown that there is a tremendous adsorption lag at this temperature.

These experimental results suggest that some modification of Alyea's explanation of the upper explosion limit may be necessary in order to remove the difficulties now existing. Further experimental work may indicate the reason for these difficulties and thereby give positive support to a completely harmonious theory.

It may be observed that a mechanism which depends on conditions in the gas phase rather than at the walls has been put forward by Semenov.[8] It later received the support of Hinshelwood and his school.[3]

Summary

1. The rate of adsorption of hydrogen on quartz and Pyrex has been measured between 400 and 550° at a pressure of 760 mm.

2. Equilibrium values have been obtained on Pyrex, and have been shown to correspond to true adsorption.

3. By combining 1 and 2 it has been shown that the attainment of equilibrium requires several hours' contact of gas and surface,

4. Lack of agreement between these results and a theory advanced by Alyea to explain the upper explosion limit of the hydrogen–oxygen reaction has been indicated.

PRINCETON, NEW JERSEY

RECEIVED NOVEMBER 1, 1932
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(8) Kopp, Kovalshii, Sagulin and Semenov, *Z physik.* Chem., B6, 307 (1930).

[Contribution from the Virginia Truck Experiment Station]

Interrelation of Electrokinetic Behavior and Cation Exchange of Iron Phosphate

By Jackson B. Hester

The fact that soil colloidal materials divide themselves electrokinetically into positive and negative colloids has brought forth some of the most interesting studies and fundamental results in soil research. Since the soil colloids consist principally of silica, humus, phosphates (electronegative material) and the sesquioxides of iron and aluminum (electropositive material), many studies[1] concerning the basic properties of these materials and their combinations have been most gratifying. It has been shown[2] that the seat of base exchange in colloidal material is in the uncombined or free valence of the electronegative materials. This being the case, a combination of materials in a reaction unfavorable for mutual precipitation of the positive and negative colloidal material should give a maximum base exchange capacity for a specific colloid. This paper is a presentation of data attempting to establish this point.

A series of seven precipitations of iron phosphate varying from the distinctly electropositive precipitate to the distinctly electronegative precipitate was made in the following manner. Five millimoles of iron chloride together with hydrochloric acid to produce the acid reaction were diluted to one liter; 10 millimoles of sodium hydrogen phosphate (dibasic) and the sodium hydroxide necessary to produce the alkaline reaction were diluted to one liter and added to 500 cc. of molar ammonium chloride; the two solutions were mixed together in large containers by pouring from one container to the other and back again in rapid succession several times and finally stoppering the mixture in a three-liter Erlenmeyer flask. The ammonium chloride was added to ensure complete precipitation of the colloid.

The above mixtures were allowed to stand overnight and the supernatant liquid was siphoned off. Then the total mass was thrown on a filter paper and the precipitate was allowed to become air dry for further analysis. The cation exchange capacity was determined by saturating the complex to P_H 7.0 with calcium acetate and replacing the calcium with ammonium chloride.

The composition of each precipitate was determined by analysis and is reported in Table I as molecular formulas.

The water represented in the molecular formula was determined by igniting the material, dried at 108°, at a dull red heat until a constant weight was obtained. The M_2O represents the cation exchange capacity

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(1) Mattson, *J. Phys. Chem.*, 32, 1532–1552 (1928); *Soil Sci.*, 30, 459–495 (1930); 31, 57–77 (1931).

(2) Mattson, Soil *Sci.*, 31, 311–331 (1931); 32, 343–365 (1931); 33, 75–94 (1932)

TABLE I

MOLECULAR FORMULAS BY CHEMICAL ANALYSIS AND THE *P*H VALUE AT PRECIPITATION OF SEVEN IRON PHOSPHATE PRECIPITATES

5 Millimoles of $FeCl_3$, 10 millimoles of Na_2HPO_4, and 500 millimoles of NH_4Cl used in each case with the acid and alkali added to give a final volume of 2500 cc.

No.	Millimoles of HCl and NaOH added	*P*H of medium	Molecular formula F_2O_3	P_2O_5	H_2O	M_2O
1	5	3.1[a]	1	0.946	3.845	0.917
2	2.5	3.7	1	.939	3.645	.864
3	0	4.4	1	.928	3.316	.838
4	5	6.8	1	.895	3.325	.956
5	10	7.5	1	.841	5.165	1.111
6	20	8.0	1	.780	2.803	0.964
7	40	8.7	1	.568	2.630	.734

[a] Determined colorimetrically.

of the colloid. The colloid was air dried before the cation exchange capacity was determined.

System Number 3[3] represents the isoelectric mixture; Numbers 1 and 2 arc the most highly electropositively charged colloids. Numbers 4, 5, 6 and 7 are the electronegatively charged colloids.

The formulas in Table I show that there is a slight decrease in the phosphate content of the molecule as the PH value of the medium rises. There is, however, only a small change in the phosphate content of the first five precipitates, whereas there is a rather large decrease in the phosphate content of the last two precipitates.

The cation exchange capacity of the colloidal complex is influenced by the reaction of the medium in which it is precipitated. Thus, the isoelectric colloid has a lower cation exchange capacity than the electropositive colloid. The exchange capacity of the electronegative precipitates increases progressively until above reaction PH 7.5, after which it decreases, due no doubt to the decrease in phosphate content.

The slight increase of the phosphate ion in the colloid on the electropositive side of the isoelectric point hardly accounts for the increase in the exchange capacity, nor does the increase of phosphate account for the increase in the molecular held water. On the electronegative side of the isoelectric point the phosphate content of the colloidal complex continues to decrease slightly till a reaction of PH 7.5 is reached and above this point it decreases rapidly.

Figure 1 shows the relation of the charge on the colloidal particle and the base exchange capacity of the colloid. The cation exchange capacity is calculated on the basis of 5 millimoles of PO_4 and shown in curve C.

Again, in order to show further that the reaction at which the material

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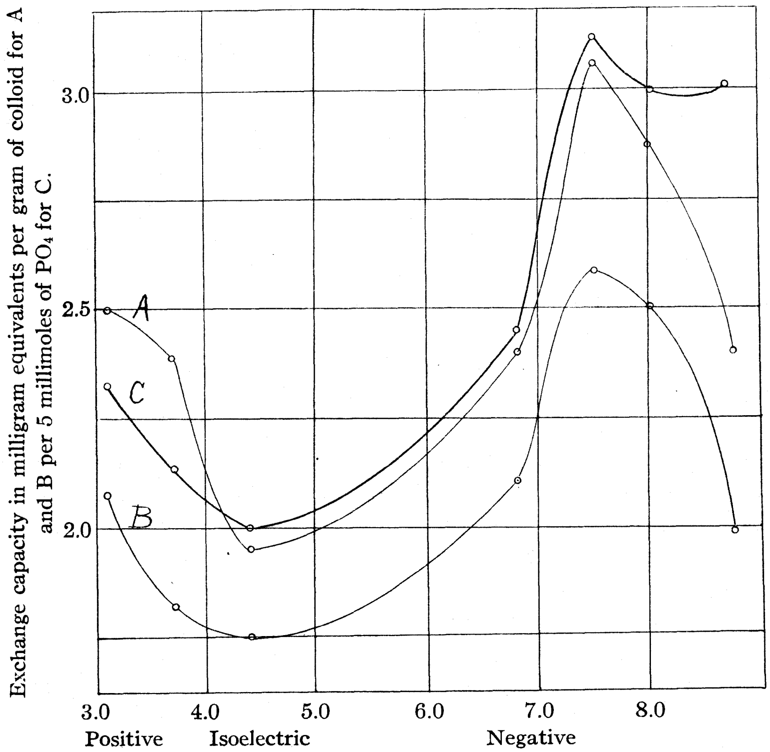
(3) The cataphoretic measurements of the particles were not actually made, but previous work by Dr. Sante Mattson [*Soil Sci.*, **30**, 459–495 (1930)] showed the particles to carry the charges mentioned The author had the privilege of starting this work in Doctor Mattson's laboratory. The results were repeated and confirmed at the Virginia Truck Experiment Station

was precipitated influenced the exchange capacity as ordinarily estimated, the calculations were made on the basis of one gram of air-dried material and material dried at 108°. The data are also presented in Fig. 1 as curves A and B.



PH value at precipitation: A, based on material dried at 108"; B, based on material air dried; C, based on 5 millimoles of PO_4.

Fig. 1.—The cation exchange capacity of iron phosphate.

In connection with the molecularly held water (that water given off by ignition), it will be noted that the water content of the precipitate follows somewhat the same trend as the base exchange capacity. The two curves also show upon interpretation that the water lost from the air-dried material upon heating to 108° is greatest where the cation exchange capacity is the largest.

A survey of the data in Table I and the curves in Fig. 1 shows how the reaction of the medium in which a precipitation takes place alters the combination of the two oppositely charged colloidal materials. At the isoelectric point the two oppositely charged materials carry equal charges and a mutual precipitation takes place. This more complete union makes the isoelectric colloid the more stable colloid. Since the neutralization of the charged colloids is the most complete at the isoelectric point, the free valence is at a minimum, the seat of the base exchange capacity is then at a minimum, and the quantity of combined water is at a minimum for a given colloid.

Summary

The cation exchange capacity of seven iron phosphate precipitates varying from the electropositive to the electronegative combinations was investigated. The data presented indicate that high base exchange accompany high electrokinetic potential, whereas low base exchange is characterized by a low electrokinetic potential.

NORFOLK, VIRGINIA RECEIVED NOVEMBER 9, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Atomic Weight of Lead from Bedford Cyrtolite

BY GREGORY PAUL BAXTER AND CHESTER M. ALTER

The lead–uranium ratio in a specimen of cyrtolite from Bedford, N. Y., U. S. A., has recently been determined by Muench[1] to be 0.0513 (Pb 0.374, U 7.29, Th 0.0?). In estimating the age of this mineral it is important to discover by the determination of its atomic weight whether this lead was wholly derived from the disintegration of uranium. An added interest to this determination comes from the fact that the mineral is nearly if not quite free from thorium.

Since cyrtolite consists chiefly of zirconium silicate and is extremely refractory, the extraction of the lead was a matter of some difficulty. The method finally adopted after some exploration was that of treatment with hydrofluoric acid. About 1250 grams was available.

The lumps were first crushed in a previously cleaned jaw crusher. The material was then finely ground in a Quaker grinding mill which had been cleaned by grinding in it several hundred grams of marble. Prolonged digestion in 100-g. portions with hydrofluoric acid in a platinum dish followed. Removal of the hydrofluoric acid was effected by repeated evaporation with concentrated nitric acid. The portion soluble in hot dilute nitric acid was then separated from the very considerable residue of undissolved zirconium silicate.

The lead was next separated and purified by the following processes: (1) double precipitation as sulfide; (2) solution of the sulfide in nitric acid and precipitation of lead chromate in ammonium acetate solution; **(3)** solution of the chromate in nitric acid and precipitation of lead sulfate; (4) conversion of the sulfate to carbonate by boiling with sodium carbonate

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[1] Muench, *Am J. Sci.*, **21**, 366 (1931).

solution; (5) solution of the carbonate in nitric acid and three recrystallizations of the nitrate from concentrated nitric acid in quartz; (6) conversion of the nitrate to chloride by repeated evaporation with hydrochloric acid in quartz; (7) recrystallization of the chloride, once in quartz and three times in platinum; (8) distillation of the chloride in a current of hydrogen chloride in a quartz tube. All the acids used in the foregoing operations were freshly distilled and other reagents were proved to be free from lead before use. All the material resulting from this purification was used in Analysis 1.

As soon as the first analysis was completed, the resulting lead nitrate solution was evaporated, freed from silver with a small amount of hydrochloric acid and, after combination with the mother liquors of the first set of crystallizations and conversion to nitrate, the product was three times crystallized as nitrate in quartz and three times as chloride, once in quartz and twice in platinum. The final step was distillation in hydrogen chloride as before. This material was used in Analysis 2.

For the next analysis (3) the combined lead salt was five times crystallized as nitrate in quartz, and five times as chloride, twice in quartz and three times in platinum.

The final analysis with cyrtolite lead was performed with material which had been three times crystallized as nitrate and four times as chloride.

For purposes of comparison experiments were carried out with common lead and with lead extracted from Swedish kolm by Baxter and Bliss.[2] Ordinary lead nitrate was three times crystallized from nitric acid in quartz and after conversion to chloride the latter was crystallized once in quartz and three times in platinum. The kolm lead was crystallized six times as nitrate and six times as chloride. All the samples were finally distilled in a current of hydrogen chloride in a quartz tube.

The distilled lead chloride was prepared for weighing by fusion in a current of hydrogen chloride while contained in a weighed quartz boat in a quartz tube. After cooling in nitrogen, the boat and contents were transferred to a weighing bottle by means of a Richards bottling apparatus. In Analysis 4 the fusion atmosphere was a mixture of one part hydrogen chloride to ten of nitrogen.

Comparison of the lead chloride with silver was effected nephelometrically. In Analyses 2 and 3 the lead chloride solution was added to the silver nitrate solution; in all other analyses the reverse method of precipitation was employed. In three analyses the end-point was approached from one side, in three from the other. The precipitation and testing were both done at room temperature. In Analyses 2 and 7, after the end-point had been found at room temperature, the solutions were cooled with ice. When again tested nephelometrically no change could be detected.

(2) Baxter and Bliss, THIS JOURNAL, 52, 4848 (1930).

Because of the small amounts of material available in the experiments with cyrtolite and kolm lead the weighing bottle, boat and bottling apparatus were made of small size in order to increase the accuracy of weighing.

The concentration of the solutions before precipitation was not far from 0.02 normal, and the total volume of the solutions in the cyrtolite experiments about one liter. Under these circumstances the uncertainty in determining the end-point with the nephelometer is not over 0.05 mg. of silver or the equivalent amount of chloride, a quantity which would affect the observed atomic weight of lead by 0.02 unit in an experiment in which somewhat less than one gram of lead chloride was used. The range of the cyrtolite analyses is about double this, but three of the four analyses are essentially identical.

Three different specimens of silver were employed, all of which had been purified by the same processes.[3]

All weighings were made by substitution with calibrated weights. Vacuum corrections of +0.058 mg. and −0.031 mg. per gram, respectively, were applied to the air weights of lead chloride and silver.

THE ATOMIC WEIGHT OF LEAD

Ag = 107.88 Cl = 35.457

Analysis	*Sample* of $PbCl_2$	$PbCl_2$ *in* vacuum, g.	Ag *in* vacuum, g.	Ag *added,* g.	Corr. wt. of Ag, g.	*Ratio* $PbCl_2$: 2Ag	At. *wt.* *of* Pb
1	Cyrtolite	0.99965	0.77881	+0.00025	0.77906	1.28315	205.938
2	Cyrtolite	.99219	.77286	+ .00039	.77325	1.28314	205.936
3	Cyrtolite	.76907	.59951	− .00005	.59946	1.28294	205.893
4	Cyrtolite	.73596	.57368	− .00010	.57358	1.28310	205.928
					Average	1.28317	205.924
5	Common	2.47843	1.92263	+ .00011	1.92274	1.28901	207.203
6	Common	2.80252	2.17405	.00000	2.17405	1.28908	207.218
					Average	1.28905	207.211
7	Kolm	3.42063	2.66525	− .00010	2.66515	1.28347	206.007

The analyses of common lead chloride were performed first and although the average atomic weight found is slightly lower than the more probable value, 207.22, the difference was so small that it did not seem a matter of concern. Since the results of the experiments with cyrtolite lead were unexpectedly low, the experiment with kolm lead was undertaken. The outcome of this experiment is reassuring, since Baxter and Bliss[2] obtained an almost identical result, 206.013.

One conclusion seems certain, that the cyrtolite lead is essentially free from common lead so that the lead–uranium ratio obtained by Muench may be confidently employed in computing the age of the mineral.

The explanation of the low value for cyrtolite lead is not so obvious. Aston finds the lead isotopes integral with the mercury isotopes, which on the physical scale, O^{16} = 16.0000, were found to have values 0.01 per cent.

(3) See *Baxter and* Ishimaru, THIS *JOURNAL*, **51, 1730 (1929).**

higher than integral, the accuracy claimed being 0.01 per cent. In converting from the physical to the chemical scale, if the higher factor of Mecke and Childs, 1.00022, is used, the atomic weight of radium lead falls between 205.96 and 206.00. However, if the latter is always accompanied by actinium lead, Pb^{207}, in the proportions found in Katanga lead by Aston[4] (93.3:6.7) the average atomic weight of uranium lead should be 0.07 unit higher, a difference far outside the apparent accuracy of our experiments. **This** suggests the possible presence in uranium lead of lead isotopes of lower atomic mass than 206. An alternative is that the atomic weight of lead as found by us is too low, or that the packing fraction of lead determined with the mass spectrograph is incorrect.

The experimental result of this research is that the atomic weight of uranium lead from a specimen of cyrtolite is 205.92 ± 0.02.

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[4] Aston, *Nature*, **129**, 649 (1932).

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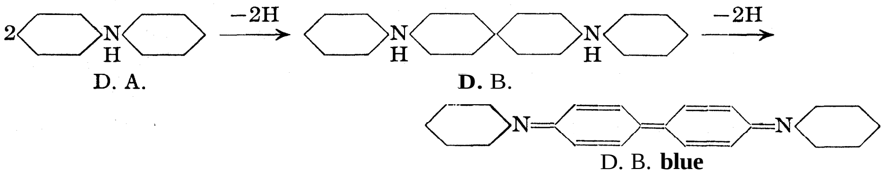
Diphenylamine Sulfonic Acid as a Reagent for the Colorimetric Determination of Nitrates

BY I. M. KOLTHOFF AND G. E. NOPONEN

Since first suggested by E. Kopp,[1] the use of diphenylamine for the colorimetric determination of nitrates has been studied by numerous investigator~.~Diphenylamine, mainly for the following reasons, is far from being an ideal reagent in the colorimetric determination of nitrates.

1. The blue color developed by nitrate in the presence of much sulfuric acid and some hydrochloric acid is to be attributed to the formation of an oxidation product of diphenylbenzidine, the latter being the first oxidation product of diphenylamine.



Diphenylamine therefore is not a specific reagent for nitrate, but the blue color is also developed by other oxidizing agents, such as ferric iron, nitrite, dichromate, etc.

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(1) E. Kopp, *Ber.*, 6, 284 (1872).

(2) See especially the more extensive investigations of Tillmans and Sutthoff, Z. *anal. Chem.*, **50**, 473 (1911); L. Smith, *ibid.*, **56**, 28 (1917); Riehm, *ibid.*. 81, 353 (1930); for bibliography compare J. H. Yoe, "Photometric Chemical Analysis," Vol. I, Colorimetry, John Wiley and Sons, New York, 1928, pp. 638–659.

2. The intensity of the blue color developed strongly depends upon the ratio of diphenylamine and nitrate in the reacting mixture. The concentration of the blue holoquinoid oxidation product decreases with increasing excess of diphenylamine, because part of the nitrate is consumed in the oxidation of the reagent to the colorless diphenylbenzidine. Still the use of the latter substance as a reagent does not seem to offer special advantages, as may be inferred from a study by H. Riehm.[3]

3. The blue oxidation product is not stable; in addition, it reacts on standing with diphenylbenzidine with formation of a green slightly soluble meriquinoid. Therefore the intensity as well as the shade of the color changes with time of standing.

4. The nitrate in the reacting mixture is reduced to nitrogen oxide (NO), the latter being partly oxidized by oxygen from the air to NO_2 which reacts again with the indicator with the formation of diphenylbenzidine blue and NO. The latter again is reoxidized, etc. Therefore the concentration of the blue dye is much larger than corresponds to the simple stoichiometric reaction between nitric acid and diphenylamine; hence the color intensity after a certain time of standing is much larger with nitrates than with equivalent amounts of other oxidizing agents. This explains why the reaction is much more sensitive for nitrates than for other oxidizing agents and also why the way of mixing the acid nitrate solution with the reagent has a pronounced influence upon the intensity of the color and its development with time of standing (see experimental part).

5. Other factors, such as temperature during the mixing and at the time of standing, the concentration of sulfuric acid and chloride in the reacting mixture, shaking after mixing, and even the size of the tubes or vessels used affect the intensity of the color. Although various factors can be controlled by working under standardized conditions, it is evident that it will be hard to get reproducible results. From all this it is not surprising that no linear relation is found between the concentration of nitrate and the intensity of the color developed (Beer's law).

The advantages of diphenylamine sulfonic acid as an oxidation–reduction indicator[4] suggested the possibility of using it in the colorimetric determination of nitrates. The oxidation mechanism of the sulfonic acid is similar to that of diphenylamine; therefore some of the disadvantages involved in the use of diphenylamine (or benzidine) will also occur with diphenylamine sulfonic acid as a reagent. Preliminary experiments showed that the color developed in the reaction between nitrate and the sulfonic acid is fairly stable, whereas that formed in the reaction with diphenylamine or benzidine under identical experimental conditions fades relatively rapidly.

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(3) H. Riehm, Z. anal. *Chem*, 81, 439 (1930); however, see also K. Pfeilsticker, *ibid.*, 56, 397 (1931); G. W. Monier Williams, *Analyst*, 56, 397 (1931); H. Stromberg, *Proc.* Staff Meetings *Mayo Clinic*, 7, 254 (1932).

(4) L. A. Sarver and I. M. Kolthoff, THIS JOURNAL, 53, 2902 (1931).

These experiments indicated that diphenylamine sulfonic acid might be superior to diphenylamine or benzidine in the quantitative determination of nitrates. The oxidation product formed in the strongly acid medium has a bluish-violet color, whereas diphenylamine yields an indigo-blue solution.

Experimental

Materials Used.—C. P. products of potassium nitrate and potassium chloride, both recrystallized twice, and nitrogen-free sulfuric acid were used.

Sodium Diphenylamine Sulfonate.—Standard solution 0.006 molar This solution was prepared by dissolving 0.512 g. of the barium salt[4] in about 125 cc. of water. To this solution was added 0.117 g. of sodium sulfate (anhydrous) dissolved in a little water, and the barium sulfate formed filtered off. The filtrate was diluted with water to 250 cc. Various dilutions of this standard solution have been used in the experimental work.

Diphenylamine, Eastman Kodak Company product.

The conditions which affect the reproducibility and the intensity of the colored product formed in the reaction between nitrate and the reagent were systematically studied.

Effect of Method of Mixing.—The object of this set of experiments was to find a way of eliminating the uneven heating caused by heat of dilution of sulfuric acid in mixtures containing the indicator Two series of experiments were run, one in small Erlenmeyer flasks, the other in test-tubes. Each sample contained 1 cc. of 0.0003 molar diphenylamine sulfonate (standard solution 1:20), 1 cc. of a nitrate solution containing 1 mg. of NO_3 and 18 g of potassium chloride, respectively, per liter. To each mixture were added 2, 3, 4, 5, 6 and 7 cc. of sulfuric acid, respectively. The formation of colors with respect to sulfuric acid concentration was quite irregular, but the two series as a whole showed that the mixtures in Erlenmeyer flasks were lighter in color than those in the corresponding test-tubes A variation of the chloride and indicator concentration did not change the order of the effect. Similar results were obtained with diphenylamine instead of diphenylamine sulfonate as an indicator. In order to find a procedure yielding reproducible results, the methods of mixing the nitrate, indicator and acid solutions were varied systematically. The best results were obtained according to the following procedure: to an aqueous solution containing the nitrate and a suitable amount of potassium chloride a measured volume of sulfuric acid was added, the mixture after shaking cooled to room temperature, two drops of indicator (standard solution) dropped in and the whole mixed by careful stirring. By this method, which was applied in the later work, the uneven heating of the reaction mixture was eliminated and reproducible results were obtained.

Effect of Concentration of Sulfuric Acid.—It was found that the sensitivity of the reaction increases with the sulfuric acid concentration in the mixture. If the acid concentration in the reaction mixture was lower than 50%, the sensitivity of the reaction became too small and the color formation very slow. A small variation of the acid concentration in the neighborhood of 50% did not affect the reproducibility of the colors.

Effect of Concentration of Potassium Chloride.—The presence of chlorides is essential for obtaining the highest sensitivity. A concentration of 10 g. per liter of potassium chloride in the nitrate solution to be investigated was found to be a satisfactory amount. A change in this chloride content within 20% was without influence upon the intensity of the color.

Effect of Concentration of Diphenylamine Sulfonate.—If the concentration of nitrate was kept constant in a series of solutions and that of diphenylamine sulfonate varied, the intensity of the color produced increased to the point where nitrate and indicator were present in equivalent amounts. With an excess of reagent the intensity of color produced became less as the excess was increased. The stability of the color was the greatest in the solutions in which the nitrate and diphenylamine sulfonate were present in approximately equivalent quantities. In the final procedure the concentration of the reagent is kept constant in a series of standards and unknowns.

Effect of Temperature.—Experiments showed that regular and reproducible results were obtained when the indicator was added to the acid nitrate–chloride mixture at room temperature.

If the mixtures were heated above room temperature irregular results were obtained and the colors were less intense than if developed at ordinary temperature.

Relation between Color and Nitrate Concentration.—From the above it is evident that there will not be exact proportionality between the intensity of the color produced and the nitrate content of the mixture. In the final procedure the use of a series of standards (0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg. nitrate per liter) is recommended. In this range of concentrations there is sufficient proportionality between any unknown and the closest two standards to make a fairly accurate determination. The proportionality is most linear when the colors are first formed, and decreases as the solutions are allowed to assume deeper colors; this is especially true at the higher concentrations of the range. The changes taking place on standing are caused mainly by the effect of oxygen from the air (see introduction in this paper), irregular results being obtained with slight changes of conditions.

For demonstration of the time effect some experimental figures are offered in Table I. The solutions were prepared according to the standard procedure given in this paper, and comparisons made in a colorimeter.

TABLE I

EFFECT OF TIME OF STANDING ON COLOR INTENSITY

Solutions compared, NO_3 per liter	Theoretical ratio	Found, ratio after minutes							
5 and 4 mg.	1.25	3	5	10	15	20	30	90	
Ratio		1.19	1.19	1.19	1.18	1.14	1.11	1.08	
4 and 3 mg.	1.33	3	5	10	15				
Ratio		1.35	1.31	1.20	1.10				
3 and 2 mg.	1.5	2	5	10	15	30	60		
Ratio		1.7	1.53	1.48	1.43	1.30	1.18		
2 and 1 mg.	2.0	5	15	20	30	35	40	50	65
Ratio		2.65	2.4	2.25	2.05	1.98	1.90	1.82	1.7
1 and 0.5 mg.	2.0	5	20	40	55	70			
Ratio			2.0	1.86	1.7	1.68			

These data show that the best time to make comparisons varies with the concentrations of the solutions under comparison. Generally it was found that comparisons should be made as soon as colors were intense enough to allow their matching in a colorimeter. Incidentally it may be mentioned that the violet colors are much more stable than the blue ones obtained with diphenylamine or diphenylbenzidine as an indicator.

Procedure.—A series of standards is prepared each containing 10 g. of potassium chloride and 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 mg. of nitrate ion, respectively, per liter. To the aqueous solution of the nitrate to be analyzed is added potassium chloride to a concentration of 8–12 g.

per liter. If one does not know the approximate concentration of the unknown, a preliminary experiment with standards containing 0.5, 1.0 and **3.0** mg. of nitrate per liter is run.

The mixtures are prepared in the following way: to 10 cc. of the nitrate–chloride solution is added 10 cc. of sulfuric acid from a pipet. Immediately after addition of the acid the flask is put into cold water and stirred sufficiently to mix its content. After cooling to room temperature 0.1 cc. of a 0.006 molar sodium diphenylamine sulfonate solution is added and the whole carefully mixed. The colors are compared in a colorimeter as soon as the more dilute of the two standards between which the unknown appears to belong has become sufficiently colored. As already mentioned, there is no exact proportionality between intensity of color and nitrate concentration. Therefore the method of calculating the nitrate concentration of the unknown is an empirical one. Suppose the unknown was found between 2 and 3 mg.; then with the **3** mg. standard set at a reading of 20, the 2 mg. standard read *35* and the unknown 30. The concentration of the unknown then is equal to

$$2 + \frac{35 - 30}{35 - 20} = 2.33 \text{ mg. per liter}$$

After the preliminary series has given an approximate value the procedure just given is repeated with the unknown and its two closest standards. This determination gives an accuracy of the order of 5% as shown by the data in Table II.

TABLE II

COLORIMETRIC NITRATE DETERMINATION

NO_3 present, mg per liter	NO_3 found, mg. per liter	Relative error in %	NO_3 present, mg. per liter	NO_3 found, mg per liter	Relative error in %
0.32	0.34	+5	1.50	1.60	+7
.48	.47	−2	2.80	2.72	−3
.47	.50	+6	3.50	3.54	+1
.70	.70	0.0	3.68	3.65	−1
1.40	1.50	+7	4.50	4.47	−1

Interfering Substances.—Since diphenylamine and its derivatives act as oxidation–reduction indicators in the nitrate test, all oxidizing agents with high enough oxidation potential will react with the indicator. The sensitivity of diphenylamine sulfonic acid for ferric iron amounts to 2 mg. of Fe^{III} per liter, if the standard procedure is applied. Hydrofluoric acid does not eliminate the interference by ferric iron. Most oxidizing agents, however, can be easily separated from nitrate or made harmless by proper reduction. Of great practical importance is the interference by nitrite; the sensitivity toward this ion according to the standard procedure is 0.2 mg. of NO_2 per liter. Tillmans and Sutthoff[2] have recommended making nitrous acid harmless by the addition of urea. This procedure has been applied by various authors; however, it was found by us that the excess of urea interferes very strongly with the color development of small amounts of nitrate and gives rise to quite erroneous results. This is true with diphenylamine as well as diphenylbenzidine and diphenylamine sulfonic acid as reagents. The method therefore should be eliminated from the literature. It was also found that hydrazoic acid interferes strongly. The reason probably is that urea as well as hydrazoic acid reacts with the nitrous acid formed in the reoxidation of nitric oxide by oxygen from the air. Good results were obtained by another method, also recommended by Tillmans and Sutthoff, in which the nitrite is removed by boiling with ammonium chloride:

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

To 100 cc. of solution containing nitrate and no more than 10 mg. of nitrite per liter is added *0.5* g. of ammonium chloride. The mixture is boiled down to a volume of 25 cc. and made up with water and 0.5 g. of potassium chloride to 100 cc. Sodium nitrite C. P. was recrystallized twice; solutions of this salt containing 10 mg. of NO_2^- per liter were treated according to the above procedure and did not develop any color with diphenylamine sulfonate when treated according to the standard procedure after boiling. Similar experiments were made with solutions containing 10 mg. of nitrite per liter and quantities between 0.5 to 5 mg. of nitrate per liter. The colors developed were exactly the same as those developed in nitrate solutions of corresponding strengths in the absence of nitrite.

Summary

Sodium diphenylamine sulfonate can be used as a reagent in the colorimetric determination of nitrates and has advantages over diphenylamine or diphenylbenzidine as reagents. **A** procedure has been developed which allows the determination of 0.001 to 0.05 mg. of nitrate in 10-cc. samples with an accuracy of 5%. The factors affecting the reproducibility of the color formation have been studied systematically. Nitrite interferes with the determination and has to be removed by boiling with ammonium chloride. Urea cannot be used since its excess interferes with the color formation. The same is true with diphenylamine and diphenylbenzidine as reagents.

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The Volumetric Determination of Nitrates with Ferrous Sulfate as Reducing Agent

BY I. M. KOLTHOFF, E. B. SANDELL AND B. MOSKOVITZ

The only accurate method for the volumetric determination of nitrate is based on its reduction to ammonium or ammonia and distillation of the latter according to standard procedures. Other methods based on the quantitative determination of the oxidizing power of nitrate in strongly acid medium have been proposed in the literature,' but most of them require special apparatus, are time consuming, not very accurate and the results are seriously affected by the presence of air. In addition many reducing agents do not react in a simple stoichiometric way with nitric acid, but yield mixtures of oxides corresponding to various steps of oxidation of nitrogen. In the present work attempts were made to use hydrazine sulfate, arsenious oxide and antimony trichloride as reducing agents, but with unsuccessful results, the reaction mechanisms being very complicated and affected by slight changes in experimental conditions. The iodimetric method based on the quantitative reduction of nitric acid to nitric oxide by hydrogen iodide has been advocated repeatedly in the literature but cannot be recommended, since even traces of oxygen have a detrimental affect upon the results. Therefore it was decided to make a systematic study of the well-known reaction between nitric acid and ferrous iron, the latter being able to reduce the nitrate quantitatively to nitric oxide. The quantitative application of this reaction originated with Gossart,[2] who made it the basis of a direct titration using potassium ferricyanide as an outside indicator. The method yields only approximate results and has been modified by various authors. Recently L. Szebellédy[3] has shown that the appearance of the pink color of the ferrous–nitrogen oxide complex can be used as an indication of the end-point, but his procedure cannot be used for an accurate determination of nitrate. Pelouze[4] recommended the use of an excess of ferrous iron, titrating the latter back with permanganate. His method has been investigated and modified by various authors[6] but has not become a standard procedure, mainly for the following reasons: (a) the reaction between nitrate and ferrous iron

$$3Fe^{++} + NO_3^- + 4H^+ \longrightarrow 3Fe^{+++} + NO + 2H_2O$$

proceeds relatively slowly. Even in strongly acid medium in the presence of much hydrochloric acid a long period of boiling is required for the com-

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(1) For a fairly complete review of the methods previous to 1913, see H. Beckurts, "Die Methoden der Maszanalyse," Verlag Fr. Vieweg- und Sohn. Rraunschweig, 1913.

(2) Gossart, *Compt. rend.*, 24, 21 (1847).

(3) L. Szebellédy, *Z. anal. Chem.*, **73,** 145 (1928); **74,** 232 (1928).

(4) Pelouze, *Ann. chim. phys.*, [3] 20, 129 (1847).

(5) See Beckurts. Ref. 1, p. 522.

pletion of the reaction. (b) Nitric oxide is easily oxidized by oxygen and therefore precautions must be taken to exclude air during the reaction. (c) A strongly acid solution of ferrous iron is fairly rapidly oxidized by air.

In the following a simple procedure, based on the reaction between nitric acid and ferrous iron, has been developed which gives accurate and reproducible results

Experimental

Reagents and Chemicals Used

Potassium nitrate C. P. twice recrystallized from water and dried at 120°.

0.18 *N* ferrous ammonium sulfate C. P. in 1 *N* sulfuric acid. A brief study of the influence of the acid concentration upon the stability (air oxidation) of ferrous iron solutions was made. Solutions of ferrous iron in 0.05, 0.1, 0.2, 0.5, 1 and 2 N sulfuric acid, respectively, were allowed to stand in partly filled glass-stoppered bottles. They were titrated at intervals of a week over a period of three to five weeks. It appeared that the solution in 1 *N* sulfuric acid was most stable. It is recommended, however, that the solution of ferrous ammonium sulfate be standardized each day before use. The use of 0.18 *N* ferrous iron is most convenient in working with quantities of potassium nitrate ranging from 0.080 to 0.22 g. when back titration is made with 0.1 *N* dichromate.

01 *N* potassium dichromate (a weighed amount of the pure salt made up to volume).

1% ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in water.

1% solution of barium diphenylamine sulfonate in water as indicator in the titration of ferrous iron with dichromate. Diphenylamine and diphenylbenzidine can be used as well.

Sodium bicarbonate C. P. (tested for nitrate and other impurities which may have an oxidizing action).

C. p. hydrochloric acid, sulfuric acid and phosphoric acid.

In the first experiments mixtures of potassium nitrate with sulfuric acid or hydrochloric acid or both, from which the air had been removed, were boiled with excess ferrous sulfate in Erlenmeyer flasks, Bunsen valves being used to prevent entrance of air, until reduction was complete; after cooling and dilution with water, the ferrous iron remaining was titrated with dichromate. Solutions containing hydrochloric acid were reduced with greater speed than those containing sulfuric acid, but under all conditions boiling for more than half an hour was required to accomplish quantitative reduction of the nitrate. Therefore the effect of various substances on the rate of reaction was studied. It appeared that molybdate acts as a powerful catalyst in the reaction between nitrate and ferrous iron in strongly acid medium. Later it was found that Hac and Netuka[6] have made use of the same catalyst in the gasometric determination of nitrate with ferrous chloride as reducing agent.

After a systematic study the following volumetric procedure was developed.

Apparatus.—The apparatus adopted consisted of a 250-cc. Erlenmeyer flask fitted with a two-holed rubber stopper. A medicine dropper of 3 cc. capacity previously filled with ammonium molybdate solution was inserted in one of the holes and, in the other, a rubber tube leading to a saturated solution of sodium bicarbonate contained in a beaker. An Erlenmeyer flask with ground-glass stopper and dropping funnel can be used instead of the apparatus described.

The apparatus permits the addition of the catalyst after all the air has been expelled by boiling; the tube leading to the bicarbonate solution prevents the escape of irritating

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(6) Hac and Netuka, *Coll. Czechoslov. Chem. Comm.*, **1**, 521 (1928). *Cf.* R. Hac, *Eighth Intern. Congress of Applied Chem.*, **1**, 207 (1912).

hydrochloric acid fumes into the atmosphere of the room during boiling and permits cooling the flask in a carbon dioxide atmosphere.

Procedure.—A 0.1- to 0.2-g. sample of nitrate is introduced into the 250-cc. Erlenmeyer flask; 25 or 50 cc. 0.18 N ferrous iron solution are added (an excess of approximately 50% of ferrous iron is recommended) and 70 cc. 12 N hydrochloric acid. Then 3 to 5 g. of solid sodium bicarbonate is added carefully in small portions to displace the air from the flask and immediately thereafter the flask is closed with the stopper, from which a rubber tube leads to a suspension of 50 g. of sodium bicarbonate in 100 cc. of water. The dropper fitted into the other hole of the stopper contains **3** cc. of **1%** ammonium molybdate solution. The solution is heated and the catalyst added after two or three minutes' boiling. The boiling is continued for ten minutes, the sodium bicarbonate suspension then replaced with a fresh saturated solution, the flask removed from the flame and immersed in cold water. After cooling to room temperature the flask is unstoppered and 35 cc. of 6 N ammonium acetate for every 50 cc. of solution to be titrated and **3** to 5 cc. 85% phosphoric acid are added. The acetate reduces the concentration of the strong acid to between 1 and 2 N. The solution, which should have a volume of 100 to 150 cc., is slowly titrated with 0.1 *N* dichromate using 6 to 8 drops of diphenylamine sulfonate (or diphenylamine or diphenylbenzidine) as indicator. The ferrous iron solution is standardized under the same conditions as described above.

1 cc. of 0.1000 N iron is equivalent to 3.370 mg. of potassium nitrate or 2.067 mg. of NO_3.

The procedure gives results accurate to within 0.5% as may be inferred from data given in Table I.

TABLE I

VOLUMETRIC DETERMINATION OF NITRATE

Potassium nitrate		Error,	Potassium nitrate		Error,
Taken, g.	Found, g.	%	Taken, g.	Found, g.	%
0.2528	0.2526	−0.1	0.1015	0.1012	**−0.3**
.2030	.2026	− .2	.1011	.1010	− .1
.2021	.2021	.0	.1011	.1008	− .3
.2021	.2021	.0	.1011	.1011	.0
.2276	.2277	+ .05	.0910	.0909	− .1
.1539	.1534	− .3	.0811	.0810	− .1
.1210	.1212	+ .2	.0506	.0505	− .2
.1320	.1318	− .15	.0203	.0202	− .5
.1015	.1015	.0	.0202	.0202	.0

Notes.—1 The titer of the ferrous iron solution is determined in a blank under the same conditions as in the presence of nitrate. The titer is the same as found by direct titration, if air does not gain access to the solution. It may be mentioned that the air sensitivity of the ferrous iron is increased in the presence of molybdate.

2. Indication that the reduction is complete is obtained from the color of the solution during boiling. Upon addition of molybdate the solution becomes dark brown owing to the formation of the ferrous sulfate-nitric oxide complex; after two or three minutes' boiling, during which the NO is expelled, the color brightens to a reddish-orange. The orange color lightens to yellow upon cooling to room temperature.

3. Even less than the recommended amount of molybdate gives quantitative reduction within ten minutes. Experiments were made with 100 mg. of potassium nitrate in the presence of 5, 10, 20 and 30 mg. of molybdate, respectively. In all cases quantitative results were found.

4. Ions which are readily reduced by ferrous iron, such as chlorate, bromate and iodate, interfere with the nitrate determination. However, in most cases it will be possible to develop a procedure by which the oxidizing agents can be titrated without interference by nitrate, whereas the sum of nitrate and other oxidizing agent can be determined by the procedure described above. Small amounts of perchlorate do not affect the results; however, with large amounts of perchlorate slightly high results are found. With 150 mg. of potassium nitrate and 800 mg. of ammonium perchlorate the results were I to 1.5% high. It may be mentioned that manganous ion and phosphoric acid do not interfere with the determination.

The procedure described can also be applied to the determination of small quantities of nitrate between 20 and 2 mg. In the determination of very small amounts of nitrate the solutions of dichromate and ferrous iron used were four to six times more dilute than recommended in the standard procedure. The further manipulations were carried out as described above with the exception that the solution was boiled at a rate which resulted in a final volume of approximately 50 cc. After cooling, 20 cc. of 6 *N* ammonium acetate and 10 cc. of phosphoric acid were added. The solution was diluted to a volume of 100 to 150 cc. and 4 drops of indicator added for each 50 cc. of solution. The blanks were made in the same way as the determinations. With these dilute solutions the blanks should be run under the experimental conditions since a slight oxidation of the ferrous iron during the procedure results in a relatively large error.

The figures in Table II show that the results are accurate to within 3% with quantities of nitrate between 12 and 2 mg.

TABLE II

DETERMINATION OF SMALL AMOUNTS OF NITRATE

Nitrate in mg. NO_3 Taken	Nitrate in mg. NO_3 Found	Error, %	Nitrate in mg. NO_3 Taken	Nitrate in mg. NO_3 Found	Error, %
12.27	12.10	−1.4	4.91	4.86	−1.0
11.86	11.70	−1.3	2.45	2.40	−2.0
11.86	11.70	−1.3	2.45	2.38	−2.8
4.91	5.04	+2.6	2.45	2.38	−2.8
4.91	4.82	−1.8			

Summary

A procedure has been described for the volumetric determination of nitrates, in which ferrous sulfate is used as reducing agent in strong hydrochloric acid medium with molybdate as catalyst. With the aid of this procedure a nitrate determination can be made in twenty minutes. With quantities of nitrate greater than 20 mg. the maximum error is 0.5%, the error decreasing as the size of the sample increases. Amounts of nitrate of the order of a few milligrams can be determined with an accuracy of about 2%.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heat of Vaporization of Hydrogen Fluoride

BY J. H. SIMONS AND J. W. BOUKNIGHT

The heat of vaporization of hydrogen fluoride, as calculated from the vapor pressure measurements of Simons,[1] is 6025 calories for one apparent molecular weight of the gas; and this value is approximately constant over a range of temperature. It is difficult to reconcile this fact with the results of surface tension measurements of the present authors[2] and the equilibrium between HF and H_6F_6 with a heat of dissociation of about 40,000 calories per mole of H_6F_6, as determined by Simons and Hildebrand.[3] The surface tension measurements indicate that the liquid is probably composed of molecules of H_6F_6. The heat of vaporization was determined experimentally in this investigation to ascertain whether or not it would be equal to the calculated value or differ from it by an amount equal to the heat of dissociation.

Apparatus

The apparatus is shown in the diagram. It consisted essentially of a pure silver vessel, called a vaporizer, which screwed tightly into a copper plug cemented into the ground cover of a silvered Dewar vessel. To reduce the heat conduction the connection between the copper plug and the copper outlet tube was made with a small piece of thin walled silver tube silver-soldered to both copper pieces. The copper outlet tube was connected by means of silver-plated brass screw connections to three absorption tubes. These tubes were made of copper and contained finely ground sodium fluoride. They could be removed separately and weighed. The space between the silver vaporizer and the walls of the Dewar vessel could be evacuated by means of a vacuum pumping system connected through the cover of the Dewar. The heating element consisted of a piece of copper tubing wound with asbestos-covered wire, which fitted as a plug into a well in the bottom of the vaporizer A ten-junction copper–constantan thermocouple was shellacked to a glass ring that fitted the outside of the vaporizer. The electrical leads came through cement seals in the cover of the Dewar. The Dewar vessel was located in a hand-operated air thermostat. The outside ends of the thermocouples were located in the box near the copper outlet tube. It was possible to keep the temperature of the thermostat about a degree above that inside the Dewar. This prevented the liquid from condensing in the outlet tube but at the same time reduced the conduction of heat into the Dewar through the metal wires and tube.

Experimental Procedure

The hydrogen fluoride was prepared by the method of Simons.[1] It was condensed directly into the vaporizer, which had been removed from the rest of the apparatus and placed in a freezing mixture. The outlet of the generator was a small copper tube that fitted inside the outlet tube of the silver vaporizer. Special precautions were taken to ensure that no water vapor entered the vaporizer during the condensation.

The vaporizer was screwed into place and the Dewar assembled. The space inside

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(1) Simons, THIS JOURNAL, 46, 2179 (1924).

(2) *Ibid.*, 54, 129 (1932).

(3) Simons and Hildebrand, *ibid.*, 46, 2183 (1924).

the Dewar was evacuated. When temperature equilibrium had been established with the liquid at its boiling point and the air thermostat at about a degree higher in temperature, the liquid was allowed to vaporize into the absorption tubes. By weighing the absorption tubes before and after a known length of time the amount of vaporization due to heat leak into the Dewar was determined, The actual determination was made by finding the gain in weight of the absorption tubes for a known amount of energy supplied to the heating element in a given time. This was then corrected for the vaporization due to heat leak This correction factor was determined for every run.

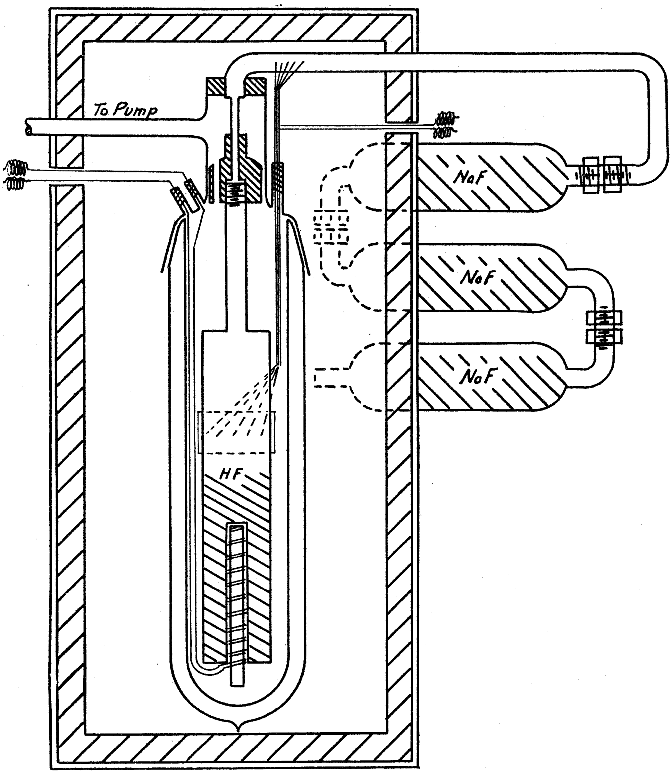

Fig. 1

Results and Discussion

The results are shown in the table. The calculated value of the heat of vaporization per gram was obtained by dividing Simons' value of the molar heat of vaporization by the apparent molecular weight determined in the vapor density determinations of Simons and Hildebrand.

The fact that the experimental values agree closely with the calculated value indicates that the actual heat of vaporization does not involve the heat of dissociation of the polymer. The agreement does, however, confirm the molecular weight determinations of Simons and Hildebrand.

HEAT OF VAPORIZATION OF HYDROGEN FLUORIDE

Duration of run, min.	Energy input		Weight HF vaporized, g.	Correction,[a] g. HF	Heat of vaporization, cal.
	volts	amp.			
76	2.08	0.145	3.4850	0.4630	109
62	2.09	.145	4.4331	1.2200	84
37	2.53	.175	2.4444	0.3901	114
41	2.62	.185	4.2252	.6540	80
20	2.46	.175	1.7732	.3188	85
17	2.83	.200	1.4280	.2713	119
The above runs represent preliminary work					
Barometric pressure 750 mm.				Average	98
30	2.88	0.200	2.4759	0.0762	103
30	2.52	.175	2.1602	.1875	96
30	2.15	.150	1.5765	.1754	99
30	1.806	.125	1.2395	.1952	93
30	1.57	.110	0.9883	.1952	94
29.25	2.14	.150	1.4279	.0815	100
Barometric pressure 748 mm.				Average	97.5

Calculated heat of vaporization per gram = 6025/63.36 = 95.

[a] This correction factor is obtained experimentally. It is the amount of hydrogen fluoride vaporized by the heat leak for the same time as the duration of the run.

Summary

The heat of vaporization of hydrogen fluoride has been determined experimentally and found to agree with the value calculated from the vapor pressure and vapor density measurements.

EVANSTON, ILLINOIS

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Notes

A Method for the Preparation of Telluric Acid

BY L. I. GILBERTSON

Gutbier, and Gutbier and Wagenknecht,[1] prepared tellurates by the oxidation of tellurium or tellurous oxide with 15% hydrogen peroxide in solution of strong alkalies. Schluck[2] oxidized tellurium with 60% hydrogen peroxide to form telluric acid.

The oxidation of tellurium and tellurous oxide is accomplished readily in sulfuric acid solution by 30% hydrogen peroxide. Best oxidation is obtained when a mixture of two volumes of 30% hydrogen peroxide with one volume of concentrated sulfuric acid (the mixture being prepared at 0°) is refluxed with the sample. The active oxidizing agent is permonosulfuric acid.[3]

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(1) Gutbier, Z. *anorg. Chem*., 42, 174 (1904); Gutbier and Wagenknecht, *ibid*., 40, 260 (1904)

(2) Schluck, *Monatsh*., **37**, 489 (1916).

(3) *Northwest Science*, **5**, No. 3, 108–109 (1932)

To prepare telluric acid, tellurium (or tellurous oxide) was refluxed with the solution of hydrogen peroxide and sulfuric acid until dissolved and active effervescence of oxygen had ceased. The solution was filtered on asbestos and evaporated to incipient crystallization. Concentrated nitric acid was added to precipitate ortho-telluric acid, which was filtered off on asbestos. After heating to decompose the remaining nitric acid, the residue was dissolved in hot water, filtered and recrystallized. Telluric acid prepared in this manner showed no qualitative indication of sulfates or nitrates.

Anal. Calcd. for oxygen to oxidize HCl, 6.97. Found, 6.95. Calcd.: tellurium, 55.54. Found, 55.56.

THE STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON

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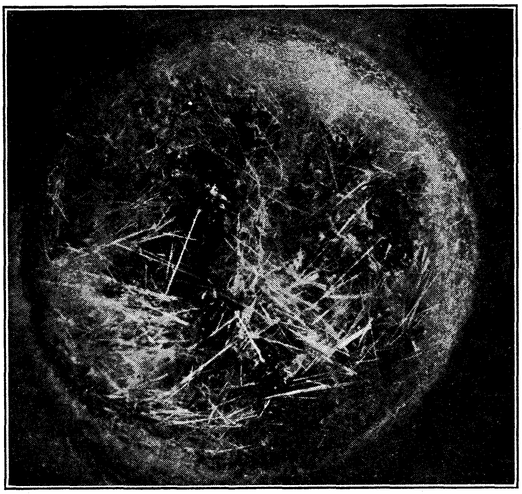
Needle-Shaped Crystals of Sodium Chloride

BY W. S. HINEGARDNER

A few weeks before the appearance of the note,[1] "Needle-Shaped Crystals of Sodium Chloride Obtained by Percrystallization," the writer noticed a thick mat of fine needle-shaped crystals covering a semi-dry silica gel which had been set aside in a beaker covered with a watch glass. Analysis for chlorine, as well as solubility and taste, indicated practically pure sodium chloride. The needles under these conditions developed usually to a length of 2–2.2 cm. The accompanying photograph shows the masses of needles that formed on the gel in one of the beakers.



Sodium chloride needles forming on fractured silica gel in a beaker.

The gel was prepared from sodium silicate solution of specific gravity 1.118, made from crystalline hydrated sodium silicate, and 3 *N* hydrochloric acid. The needles appeared after the unwashed gel had dried sufficiently to fracture. Other specimens which have since dried sufficiently produced similar masses of the same needle-shaped sodium chlo-

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[1] Henry Tauber and Israel Kleiner, THIS JOURNAL, 64, 2392 (1932).

ride crystals. The phenomenon is evidently a case of percrystallization, the outer layers of silica gel replacing the collodion membrane.

We have been unable to find the formation of needles of sodium chloride under these conditions mentioned in the literature. Experiments have been started to determine if the substitution of hydrobromic or hydriodic acid for the hydrochloric acid will give needles of sodium bromide or sodium iodide.

CONTRIBUTION FROM
THE ROESSLER & HASSLACHER CHEMICAL CO., INC.
PERTH AMBOY, NEW JERSEY

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A Beaker for Quantitative Analysis

BY G. P. BAXTER

In handling precipitates the quantitative analyst is frequently troubled as to the disposal of the stirring rod once filtration is commenced. If it is rested in the lip of the beaker, there is danger of transfer of precipitate from the lip of the beaker to the upper part of the stirring rod. If the stirring rod is rested at any other point on the rim of the beaker, it interferes with the cover glass. This difficulty may be avoided if the beaker has two lips, one of which is used entirely for pouring, the other for the stirring rod. The two lips may be distributed, of course, in any desired way, but symmetrical distribution is less convenient than unsymmetrical, for instance 90° apart, because of the difficulty of identification. If the lips are of different shape identification would be simple in any case. Beakers of this type have been found extremely convenient in quantitative analysis, and doubtless would be useful for other purposes. This idea is obviously equally applicable to glass dishes and porcelain vessels.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Aldehyde Oxidation of Toluenearsonic Acids

BY HOWARD M. PARMELEE[1] AND CLIFF S. HAMILTON

Recently, Scott and Hamilton[2] used the Bart reaction in the preparation of 4-formyl-2-nitrobenzenearsonic acid and m-formylbenzenearsonic acid. Applying Thiele and Winter's method,[3] they oxidized *p*-toluenearsonic acid to *p*-formylbenzenearsonic acid; obtaining a small yield. The preparation of p-formylbenzenearsonic acid and several ketone arsonic acids has been claimed in patents granted to Margulies[4] and again in others granted to Albert.[5] Margulies patented the derivatives of 4-formyl-2-nitrobenzenearsonic acid and 4-formyl-2-hydroxybenzenearsonic acids,[6] while Albert[7] also has been granted a patent for the latter. Streitwolf and Fehrle have been given a patent[8] covering the thiosemicarbazones of several acetyl- and formylbenzenearseno compounds, in which the authors claim that the compounds can be made either by reducing the arsonic acid to the formylarseno compound and then preparing the thiosemicarbazone, or by first preparing the thiosemicarbazone of the aldehyde arsonic acid and subsequently reducing it. Quite recently Gibson and Levin[9] have recorded the preparation of a number of derivatives of p-formylbenzenearsonic acid.

The amino aldehydes, which are the starting compounds in the previous methods of preparing aldehyde arsonic acids, are costly and difficult to prepare. They tend to react with themselves, forming "Schiff bases," and are diazotized and coupled with arsenite with difficulty. The direct method of Rosenmund[10] in which an aryl halide is treated with tripotassium arsenite, has been applied to produce certain ketone arsonic acids in a patent granted to Albert and Schulenberg.[11] It has been shown, however, by Hamilton and Ludeman[12] that the reaction leaves much to be desired. This investigation was undertaken, therefore, to ascertain if the oxidation of the toluenearsonic acids would afford a simple and easier method of preparing aldehyde arsonic acids.

The three isomeric toluenearsonic acids were oxidized with manganic oxide in sulfuric acid solution to the corresponding formylbenzenearsonic acids and isolated as the nitrophenylhydrazones. Manganese dioxide gave

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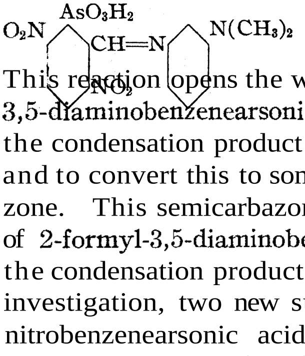
(1) Parke, Davis and Co. Fellow.
(2) Scott and Hamilton, THIS JOURNAL, 52, 4122 (1930).
(3) Thiele and Winter, Ann., 311, 355 (1900).
(4) Margulies, French Patent 562,460 (1923).
(5) Albert, German Patent 459,648 Kl$_0$ 12 (1917).
(6) Margulies, British Patent 220,668 (1923); Swiss Patent 111,939 (1922).
(7) Albert, Canadian Patent 280,834 (1928).
(8) Streitwolf and Fehrle, U. S. Patent 1,785,660 (1930).
(9) Gibson and Levin, *J. Chem. Soc.*, 2388 (1931).
(10) Rosenmund, Ber., 54, 438 (1921).
(11) Albert and Schulenberg, German Patent 468,403 (1923).
(12) Hamilton and Ludeman, THIS JOURNAL, 52, 3284 (1930).

similar yields with o-toluenearsonic acid but no unused arsonic acid could be recovered, whereas with the manganic oxide considerable amounts of the toluenearsonic acids were recoverable.

It was found necessary to maintain a high acidity in the precipitation of the substituted hydrazones of aldehydes formed by oxidation with the oxides of manganese, since, if the strongly acid solutions were neutralized or partly neutralized, manganous salts of the arsonic acids precipitated.

The oxidation with chromic anhydride, as carried out by Scott and Hamilton,[2] was repeated with increased yields, but in the case of the *p*-toluenearsonic acid, ether extraction was the only successful method for separating the arsonic acid from the chromium. Metal salts of the arsonic acid, as well as the insoluble derivatives of the reactive aldehyde group, all contained chromium, which could not be precipitated, while precipitation of the chromium as chromic hydroxide was carried out only with difficulty and when accomplished it was found that most of the organic matter was carried down in the precipitate. When *o*-toluenearsonic acid was so oxidized, the aldehyde was precipitated from the reaction mixture as the *p*-nitrophenylhydrazone, and although it contained chromium as an impurity, it could be purified.

N - (2 - Arsono - 4,6 - dinitrobenzal) - N',N' - dimethyl - p - diaminobenzene was prepared by heating 2-methyl-3,5-dinitrobenzenearsonic acid with *p*-nitrosodimethylaniline and sodium carbonate in alcohol, after the method of Sachs and Kempf[13] for the preparation of N-(2,4-dinitrobenzal)-N',N'-dimethyl-*p*-diaminobenzene. This reaction opens the way to the preparation of derivatives of 2-formyl-3,5-diaminobenzenearsonic acid, since it should be possible to hydrolyze the condensation product to give 2-formyl-3,5-dinitrobenzenearsonic acid, and to convert this to some stable derivative, for example, the semicarbazone. This semicarbazone could then be reduced to the semicarbazone of 2-formyl-3,5-diaminobenzenearsonic acid. Work on the hydrolysis of the condensation product is now being carried out. In the course of this investigation, two new substituted toluenearsonic acids, 2-methyl-3,5-dinitrobenzenearsonic acid and 2-methyl-3,5-diaminobenzenearsonic acid were prepared, the first for the condensation reaction and the second to confirm the first.



Several of the oxidation methods, which were attempted, did not give aldehydes, among these being Étard's method[14] using chromyl chloride, cerium dioxide in sulfuric acid solution, lead dioxide, and sodium hypochlorite in the presence of nickel salts. Amyl nitrite, which, according to a patent,[15] reacts with *o*- and *p*-nitrotoluene to give the oxime of *o*-

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(13) Sachs and Kempf, *Ber.*, **35**, 1226 (1902).

(14) Étard, Ann. *chim. phys*, [V] 22, 218 (1881).

(16) Meister Lucius and Bruning, German Patent 107,096 (1898).

and *p*-nitrobenzaldehyde, did not react with either the sodium salt of 2-methyl-5-nitrobenzenearsonic acid, or that of 4-methyl-3-nitrobenzenearsonic acid.

Modification of the analytical method of Cislak and Hamilton,[16] which was used to determine arsenic in this work, was found necessary, since the method failed to give accurate results, due to the sulfur dioxide which remained dissolved in the sulfuric acid unless the digestions were diluted at just the right temperature. This chance of error in the method was eliminated by diluting the digestions to 125 cc., returning the Kjeldahl flask to the flame and boiling briskly for fifteen to thirty seconds.

Experimental

Oxidation of the Isomeric Toluenearsonic Acids with Manganic Oxide.—The proportions used in the oxidations in diluted sulfuric acid were: 1 part manganic oxide. 1 part arsonic acid, and 6 parts of the sulfuric acid solution, by weight. In the oxidations carried out in concentrated sulfuric acid, 1 part manganic oxide, 1 part arsonic acid and 3.6 parts of concentrated sulfuric acid were used. The manganic oxide was mixed with the sulfuric acid solution in an ice cooled flask, and the arsonic acid added. The flask was placed in the water-bath at the desired temperature and stirred until the disappearance of the dark brown color indicated that the manganic oxide was nearly all reduced. The addition of the oxide and of the arsonic acid to the concentrated sulfuric acid was made very slowly with rapid stirring and good cooling, and the smooth brown paste placed in the refrigerator, where it hardened to a firm cake. (If these precautions are not observed, the mixture grows hot, swells and hardens too rapidly, with a lowering of the yield.) After twenty-four hours the flask was removed from the refrigerator and placed in the water-bath. Its contents could not be stirred. All reactions were continued for ten hours unless the oxide was reduced before that time, except those in concentrated sulfuric acid at room temperature, which were allowed to stand for seven days at the temperature of the laboratory.

In all cases, when the flask was removed from the water-bath, the contents were diluted with water until the concentration of sulfuric acid was 30–40%, and the unused manganic oxide filtered off and washed well with boiling water. The combined filtrate and washings were diluted with water until there was 30 cc. for each cubic centimeter of sulfuric acid originally present. The solution was filtered and treated with *p*-nitrophenylhydrazinehydrochloride solution until no more precipitate would form, allowed to stand for an hour and the practically pure nitrophenylhydrazone filtered off, washed and dried at 105°.

The unused manganic oxide from each oxidation was washed with ether, N sodium hydroxide solution, 10% sulfuric acid solution, and finally with water before drying. The unused toluenearsonic acid from each oxidation was dissolved in 40 cc. of dilute sodium carbonate solution, filtered and reprecipitated with hydrochloric acid.

The concentration of sulfuric acid was varied from 30 to 96% and the temperature varied from room temperature to the boiling point of the solution, except in the case of the 96% sulfuric acid which was not heated above 100°. The best average yield of *o*-formylbenzenearsonic acid was 24.8%, allowing for the recovered o-toluenearsonic acid, and was obtained using 96% sulfuric acid at room temperature. The greatest yield of *p*-formylbenzenearsonic acid was 11.8%, allowing for the recovered *p*-toluenearsonic acid, and was obtained using 96% sulfuric acid at 80°, while the best yield of *m*-toluene-

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(16) Cislak and Hamilton. THIS JOURNAL, **52**, 638 (1930).

arsonic acid was 7.4%, taking into consideration the recovered m-toluenearsonic acid, and was obtained using 40% sulfuric acid at the temperature of a boiling water-bath.

The *p*-**Nitrophenylhydrazones.**—The *p*-nitrophenylhydrazone of *p*-formylbenzenearsonic acid precipitated as orange flocks which coagulated to a yellow solid, insoluble in water and in ordinary organic solvents, but could be recrystallized with difficulty from glacial acetic acid. It was purified by making the solution of its sodium salt just faintly acid to litmus paper, and filtering, then acidifying the filtrate to Congo red paper with hydrochloric acid; m. p. > 250°.

Anal. Calcd. for $C_{13}H_{12}O_5N_3As$: As, 20.53. Found: As, 20.53, 20.50.

The p-nitrophenylhydrazone of o-formylbenzenearsonic acid precipitated as orange flocks which coagulated slowly at room temperature, rapidly at 60°, to a yellow solid. It was insoluble in water, but could be recrystallized from a large volume of alcohol as yellow needles; m. p. 201.5°, corr.

Anal. Calcd. for $C_{13}H_{12}O_5N_3As$: As, 20.53. Found: As, 20.45, 20.49.

The p-nitrophenylhydrazone of m-fonnylbenzenearsonic acid was an orange solid and was purified by reprecipitation from a solution of its sodium salt. It was but little soluble in organic solvents; m. p. > 250°.

Anal. Calcd. for $C_{13}H_{12}O_5N_3As$: As, 20.53. Found: As, 20.52, 20.58.

Phenylhydrazone of o-Formylbenzenearsonic Acid.—In addition to the *p*-nitrophenylhydrazone used to determine the yields, a new compound, the phenylhydrazone, was prepared as follows. Twelve grams of o-toluenearsonic acid was oxidized with manganic oxide and sulfuric acid and after removing the unused oxide from the mixture, the remaining solution was treated with concentrated ammonium hydroxide solution until a trace of permanent precipitate formed. A solution of phenylhydrazine hydrochloride, containing 2 g. of phenylhydrazine, was then added whereupon the phenylhydrazone precipitated as a yellow solid. This was suspended in 20 cc. of warm water and dissolved by adding sodium carbonate. The solution was neutralized with acetic acid, cooled in ice, and the sodium salt of the phenylhydrazone of o-formylbenzenearsonic acid precipitated as shining scales. These were filtered off, sucked as dry as possible (but not washed), dissolved in 300 cc. of water, filtered and the solution made acid to Congo red paper to precipitate the arsonic acid. This was filtered off and dried in a vacuum desiccator over phosphorus pentoxide; yield, 2.1 g. (11.8%). The substance darkened when dried at 105°, and decomposed between 131 and 137°, depending on the rapidity of heating. It crystallized from hot alcohol as small yellow prisms.

Anal. Calcd. for $C_{13}H_{13}O_3N_2As$: As, 23.42. Found: As, 23.45, 23.44.

Oxidation of o-Toluenearsonic Acid with Manganese Dioxide.—Five grams of manganese dioxide with 8.3 g. of o-toluenearsonic acid was refluxed with 50 g. of 40% sulfuric acid solution for ten hours. The unused manganese dioxide was filtered off and washed thoroughly with boiling water. The filtrate and washings were combined, diluted to 300 cc. and treated with p-nitrophenylhydrazine hydrochloride solution until no more precipitate formed. The p-nitrophenylhydrazone of o-formylbenzenearsonic acid was filtered, washed and dried at 105°, then over phosphorus pentoxide; yield, 0.8 g. (6%). A similar oxidation using 10 g. of manganese dioxide gave 0.7 g. (7%). Two reactions were carried out in bomb tubes. Both tubes contained 8.3 g. of *o*-toluenearsonic acid, 5 g. of manganese dioxide and 50 g. of 40% sulfuric acid solution and were heated for ten hours, one at 140" and the other at 155°. The first gave 0.35 g. (3%), the second gave 0.65 g. (7%).

The filtrates, from which the p-nitrophenylhydrazone was taken, were decolorized with activated charcoal and concentrated to about one-third their former volume. On cooling, there was formed a small quantity of white needles which did not melt below

260°. These portions of needles were combined and recrystallized from hot water, and proved to be o-benzarsonic acid.

Oxidation of *p*-Toluenearsonic Acid with Chromic Acid Anhydride.[17]—Thirty grams of p-toluenearsonic acid was dissolved in a solution of 120 cc. of acetic anhydride. 120 cc. of glacial acetic acid and 27 cc. of concentrated sulfuric acid, in a 500-cc. wide-mouthed flask, through the stopper of which passed a stirrer, thermometer and addition tube. The flask was cooled in ice and 24 g. of chromic acid anhydride added in small portions over a period of ninety minutes. The temperature was held at 5–10°, and the mixture stirred vigorously during the addition and for forty-five minutes thereafter. The reaction mixture was then scraped into 300 g. of ice, dissolved and allowed to come to room temperature. The solution was extracted with one 400-cc. and three 100-cc. portions of ether. The aqueous layer was treated several times by alternately adding 15 cc. of glacial acetic acid and extracting it with 75 cc. of ether. The ether extract was concentrated under reduced pressure to 100 cc., diluted with water to 250 cc., and again concentrated to 100 cc. It was then nearly neutralized with 6 N sodium hydroxide solution and filtered. The filtrate contained the p-formylbenzenearsonic acid, and from such solutions the derivatives described below were prepared. *p*-Nitrophenylhydrazone of *p*-formylbenzenearsonic acid was obtained in yields of 12% from the concentrated extract resulting from the oxidation of 15.8 g. of p-toluenearsonic acid. Phenylhydrazone of p-formylbenzenearsonic acid was obtained in 8% yields from the concentrated extract produced by the oxidation of 30 g. of p-toluenearsonic acid. One and two-tenths grams (5.7%) of the semicarbazone of p-formylbenzenearsonic acid[18] was obtained from the concentrated extract obtained by the oxidation of 15.8 g. of the arsonic acid.

Oxidation of o-Toluenearsonic Acid with Chromic Acid Anhydride.—Fifteen grams of o-toluenearsonic acid was oxidized by the method outlined for the para isomer. and the reaction mixture scraped into 200 g. of ice and dissolved. The solution was diluted to 500 cc. and allowed to come to room temperature, then treated with 60 cc. of *p*-nitrophenylhydrazine hydrochloride solution containing 2 g. of *p*-nitrophenylhydrazine. The yellow precipitate was filtered, washed, warmed with dilute sodium carbonate solution, and the insoluble part filtered off and dissolved in 10 cc. of concentrated sulfuric acid in an ice-bath. The sulfuric acid solution was poured into 300 cc. of water, whereupon a yellow precipitate in a green solution was formed. This was filtered, the precipitate washed and dissolved in dilute sodium carbonate solution, which was then combined with the original sodium carbonate filtrate. The resulting solution was made just acid to litmus paper and treated with activated charcoal while hot, then acidified to Congo red paper. The p-nitrophenylhydrazone of o-formylbenzenearsonic acid precipitated as a yellow solid; yield, 1.0 g. (4%).

2-Methyl-3,5-diitrobenzenearsonic Acid.—Using the method of Karrer,[19] 2-methyl-5-nitrobenzenearsonic acid was prepared, and 30 g. of the carefully dried product dissolved in 60 cc. of fuming sulfuric acid (20% excess sulfur trioxide) in a 200-cc. flask. To this solution 22.5 cc. of red fuming nitric acid (sp. gr. 1.6) was added in small portions. A vertical tube 70 cm. long was fitted to the flask with a ground-glass connection and the flask placed over a boiling water-bath. The water level was held just below the bottom of the flask, which rested on the rings that covered the bath. The solution was stirred through the tube and heated for four hours, then poured over six volumes of crushed ice. The 2-methyl-3,5-dinitrobenzenearsonic acid precipitated as white crystals. It was filtered off, washed with a little water, then suspended in 200 cc. of water, and concentrated ammonium hydroxide solution added with warming until all dissolved. The solution was made just acid to litmus paper with hydrochloric acid, and filtered

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(17) Scott and Hamilton, THIS JOURNAL, 52, 4122 (1930).

(18) Gibson and Levin, J. Chem. *Soc.*, 2388 (1931).

(19) Karrer, Ber., 48, 311 (1915).

warm through a mat of activated charcoal, and the filtrate acidified to Congo red paper The substance precipitated as needles; yield, 23–24 g. (65–68%) of almost pure material, which was used in this form; m. p. 201–203°. The substance crystallized in two interconvertible forms. When a hot solution was cooled rapidly, the product consisted of hexagonal plates, frequently elongated to needles, but when a cold neutral solution of the sodium salt was acidified slowly with hydrochloric acid, the plates were rectangular. The rectangular plates could also be produced by seeding a hot solution and cooling it slowly.

Anal. Calcd. for $C_7H_7O_7N_2As$: N, 9.15; As, 24.50. Found: N, 9.45; As, 24.58, 24.55.

Ammonium Salt of **2-Methyl-3,5-dinitrobenzenearsonic** Acid.—Eight grams of 2-methyl-3,5-dinitrobenzenearsonic acid was suspended in 60 cc. of water and concentrated ammonium hydroxide solution added with warming until all dissolved. The solution was then just neutralized with hydrochloric acid and cooled. Scratching the beaker with a glass rod, or seeding, caused the ammonium salt to precipitate as rhomboidal scales which were filtered off, washed with 10 cc. of water and dried at 105°. They were soluble in water and the aqueous solution gave back the 2-methyl-3,5-dinitrobenzenearsonic acid when acidified to Congo red paper with hydrochloric acid.

Anal. Calcd. for $C_7H_{10}O_7N_3As$: As, 23.20. Found: As, 23.11, 23.17.

2-Methyl-3,5-diaminobenzenearsonic Acid and its Sodium Salt.—Ten grams of 2-methyl-3,5-dinitrobenzenearsonic acid gave 3 g. (37%) of the corresponding diamino compound when reduced by the ferrous hydroxide method of Jacobs, Heidelberger and Rolf.[20] The product was precipitated as fine needles, soluble in 3 *N* hydrochloric acid solution, but insoluble in water.

Anal. Calcd. for $C_7H_{11}O_3N_2As$: As, 30.46. Found: As, 30.50, 30.48.

The sodium salt was prepared by dissolving the acid in dilute sodium carbonate solution and neutralizing the solution to litmus paper with hydrochloric acid. The sodium salt, separating as a yellow solid, was filtered off, washed with a little alcohol and dried at 105°.

Anal. Calcd. for $C_7H_{10}O_3N_2AsNa$: As, 27.96. Found: As, 28.07, 28.10.

N-(2-Arsono-4,6-**dinitrobenzal)-**N′,N′-**dimethyldiaminobenzene.**—Twenty-five grams of 2-methyl-3,5-dinitrobenzenearsonic acid and 10 g. of anhydrous sodium carbonate were placed in a 500-cc. flask with a mixture of 75 cc. of ethyl alcohol and 75 cc. of methyl alcohol. The flask was fitted with a reflux condenser and the contents refluxed on a water-bath. Carbon dioxide was evolved. After fifteen minutes refluxing, the flask was removed and 10.8 g. of *p*-nitrosodimethylaniline added, then returned to the bath and refluxed for two hours. The color of the solution changed from green to dark brown. The flask was again removed and the contents poured into an evaporating dish, where the alcohol was allowed to evaporate at 30–35°. The black solid which remained was dissolved in 300 cc. of water and a small amount of insoluble material filtered off on a mat of activated charcoal. The deep red-brown filtrate was then treated with glacial acetic acid until it was definitely acid to litmus paper and a black precipitate formed, which was filtered off and air dried; wt. 19 g. It was dissolved in dilute sodium carbonate solution and filtered then reprecipitated as before with acetic acid. This solution and reprecipitation was repeated two more times, with a final yield of 4.7 g. (13%), air dried. The product was bulky and gelatinous when freshly precipitated, and was difficult to wash on the filter. It was therefore placed in a flask with 100 cc. of water and stirred rapidly with a mechanical stirrer for one-half hour, then filtered again. When dry, its volume always diminished greatly. It was ground in a

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(20) Jacobs, Heidelberger and Rolf, THIS JOURNAL, 40, 1580 (1918).

mortar until all would pass through a 100-mesh screen and the sifted material dried several days in a vacuum desiccator over phosphorus pentoxide.

The condensation product was black, but when the solution dried it left a purple film. It was soluble in 2 N hydrochloric acid, giving a red solution. When the substance was boiled with water, acetic acid, ethyl or methyl alcohol, the liquid was colored deep purple, although it was not sufficiently soluble in these solvents for recrystallization.

Anal. Calcd. for $C_{15}H_{15}O_7N_4As$: As, 17.09. Found: As 16.85, 16.70.

Summary

1. The three isomeric formylbenzenearsonic acids have been prepared by oxidation of the corresponding toluenearsonic acid, using manganic oxide and sulfuric acid solutions, and manganese dioxide and sulfuric acid solution. The aldehydes were isolated as insoluble derivatives of the carbonyl group.

2. The oxidation of *p*-toluenearsonic acid, as carried out by Scott and Hamilton, has been repeated with increased yield of the *p*-nitrophenylhydrazone and the method applied to the oxidation of o-toluenearsonic acid.

3. Derivatives of a new arsonic acid, o-formylbenzenearsonic acid, have been prepared.

4. Two new arsonic acids, 2-methyl-3,5-dinitrobenzenearsonic acid and 2-methyl-3,5-diaminobenzenearsonic acid, have been described.

5. 2-Methyl-3,5-dinitrobenzenearsonic acid has been condensed with *p*-nitrosodimethylaniline to produce N-(2-arsono-4,6-dinitrobenzal)-N′,N′-dimethyl-*p*-diaminobenzene. This is a new way of preparing derivatives of an aldehyde arsonic acid.

6. An improvement in the potentiometric titration method for the determination of arsenic has been made.

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A New Procedure for the Duclaux Method

BY JAMES B. MCNAIR

Up to the present time no method is available which will give reliable results for the analysis of four volatile aliphatic acids by the Duclaux method. It has been found by the writer that the quantitative analysis by a chemical method of one of the four acids in the Duclaux distillate makes possible the reliable estimation of the remaining three acids by the Duclaux method. In fact the quantitative estimation of one or more acids by an accurate chemical method increases the accuracy of the results of the Duclaux method when a mixture of three or more acids is involved. In the following paper a brief outline of the new procedure will be illustrated by an example.

In the new procedure for calculating the results of an analysis of mixtures of four volatile acids, one or more acids are determined quantitatively by chemical methods and the remainder of the acids may be determined quantitatively by Gillespie and Walters' graphic method.[1]

The following acids have been used: formic acid 98–100% m. p. 6–8°, acetic acid 99.9% m. p. 16.6°, propionic acid b. p. 140–142° and n-butyric acid b. p. 161–163°, all obtained from high grade firms.

In mixtures of these four acids, formic acid may be determined by the mercuric chloride method,[2] acetic because of its resistance to oxidation may be determined by the Macnair method,[3] and propionic in the presence of acetic and formic only, by the oxalate method.[4]

For example, a mixture of 7.90 cc. of 0.1 N formic, 5.35 cc. of 0 1 *N* acetic, 4.90 cc. of 0.1 N propionic and 9.88 cc. of 0.1 N butyric acids is taken for analysis. One or more Duclaux distillations are made with the mixture, and the formic acid is determined either in the distillate or in the residue in the distilling flask by the mercuric chloride method.

The amount of formic acid in the Duclaux distillate and distillate residue is determined by the mercuric chloride method. It is found to be equal to 7.38 cc of 0.1 N. In Table I it is shown that 61.6% of the total formic acid comes over in the distillate. This amounts to 7.38 X 0.616 = 4.55 cc. of 0.1 *N*. This quantity of formic acid is subtracted from the original titer figure of the distillate, Table III; 23.30 – 4.55 = 18.75 cc. of 0.1 N.

The remainder, 18.75 cc., which consists of all the other acids except formic, is now used like the original distillate titer figure of an unknown distillate. The entire procedure is perhaps made more clear by the accompanying Table III. Let M represent the acid most volatile with

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(1) Gillespie and Walters, THIS JOURNAL, 39, 2027-2055 (1917).

(2) Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 2d ed.. 1925, Washington, D. C.

(3) D. S. Macnair, *Chem. News*, 55, 229 (1887); Fresenius, *Z.* Anal. Chem., 27, 398 (1888).

(4) McNair, THIS JOURNAL, 64, 3249-3250 (1932).

TABLE I

THE AMOUNTS OF THE VARIOUS ACIDS TO BE POUND IN THE DUCLAUX DISTILLATE (GILLESPIE, WALTERS AND MCNAIR)

Distillate, cc	Formic acid, cc	Acetic acid, cc	Propionic acid, cc	Rutyric acid cc.
10	3.4	6.4	11.2	16.4
20	7.3	13.0	22.2	31.2
30	11.5	19.7	32.7	44.8
40	16.1	26.7	42.9	56.6
50	21.3	34.1	52.7	67.3
60	26.6	41.6	62.0	76.2
70	33.0	49.9	70.9	84.0
80	40.5	58.7	79.1	90.1
90	49.6	68.7	86.7	94.8
100	61.6	79.9	93.6	97.8

TABLE II

PERCENTAGES OF TOTAL ACID CONTAINED IN 100 CC. OF DUCLAUX DISTILLATE (GILLESPIE AND WALTERS)

Distillate, cc.	Formic acid	Acetic acid	Propionic acid	Butyric acid
10	6.5	8.0	12.0	16.7
20	13.0	16.3	23.7	31.9
30	20.2	24.6	34.9	45.7
40	27.8	33.5	45.8	57.9
50	35.9	42.7	56.3	68.8
60	44.8	52.1	66.2	77.9
70	55.2	62.4	75.7	85.8
80	66.8	73.4	84.5	92.1
90	81.2	85.7	92.6	96.8
100	100.0	100.0	100.0	100.0

steam, I the intermediate, and L the least volatile with steam. In this example, $M = B$, or butyric, $I = P$, or propionic, and $L = A$, or acetic. Calculations are performed as indicated in Table III. In this table $B-R$ is the percentage of butyric acid contained in the various fractions of the Duclaux distillate, as indicated in Table II, less the figures under R in the preceding column in Table III. Similarly $B-A$ is butyric minus acetic and is obtained in a like manner from Table II; $B-P$ is determined in the same way. $(B-P)/(B-A)$ is $(M-R)/(M-L)$ when it is assumed that the mixture is one of B, P, and A.

It is now assumed that the mixture is $B + P + A$. $(B-P)/(B-A)$ and $(B-R)/(B-A)$ from Table III are plotted on graph paper as in Fig. 1. The first point is ignored in the calculations as the error in this, caused presumably by carbon dioxide, is too great. The figure shows in this instance that $l + i = 0.40$, $l = 0.28$, or 28%, the fraction of acetic acid in 100 cc. of distillate; therefore $i = 0.12$, that is, 12% intermediate acid = propionic in 100 cc. of distillate. Now M, the fraction of butyric acid in 100 cc. of distillate $I-(1 + i) = 1-0.40 = 0.60$.

TABLE III

DERIVATION OF THE VALUES USED IN FIGURE 1

Distillate, cc.	Titer cc. of 0.1 N	Formic acid,[a] cc. of 0.1 N	Other acids, cc. of 0.1 N	R[b] Table II	$B - R$	$B - A$	$\frac{B - R}{B - A}$	$\frac{B - P}{B - A}$
10	2.95	0.25	2.70	14.40	3.20	9.67	0.331	0.564
20	5.60	.54	5.06	26.99	5.99	17.08	.351	.551
30	8.15	.85	7.30	38.93	7.71	22.34	.345	.531
40	10.60	1.19	9.41	50.19	8.55	25.61	.334	.514
50	12.90	1.57	11.33	60.43	8.95	25.76	.348	.526
60	15.05	1.97	13.08	69.76	8.94	26.77	.334	.474
70	17.10	2.44	14.66	78.19	8.04	23.99	.335	.449
80	19.12	2.99	16.13	86.03	6.29	18.92	.332	.429
90	21.15	3.66	17.49	93.28	3.66	11.24	.325	.395
100	23.30	4.55	18.75	99.99				

[a] Determined by $HgCl_2$ and Table I (see text). [b] Percentages of residual acid (other acids besides formic) contained in 100 cc. of the Duclaux distillate, calculated as in Table II.

TABLE IV

THE RESULTS OF ANALYSES OF HIGH AND LOW PERCENTAGE MIXTURES OF FORMIC, ACETIC, PROPIONIC AND BUTYRIC ACIDS EXPRESSED IN CC. OF 0.1 N ACID

Taken					Found					Errors				
F	A	P	B	Total	F	A	P	B	Total	F	A	P	B	Total
2.64	2.82	3.46	2.62	11.54	2.74	2.18	3.66	2.31	10.89	0.1	−0.64	0.20	−0.31	−0.65
2.26	3.00	3.24	3.58	12.08	2.14	2.76	3.60	3.40	11.90	− .12	− .24	.36	− .18	− .18
6.95	8.25	16.17	8.41	39.78	6.94	7.43	17.25	7.86	39.48	− .01	− .82	1.08	− .55	− .30
5.27	8.65	9.80	8.10	31.82	5.30	8.20	10.34	8.18	32.02	.03	− .45	0.54	.08	.20

Now, there is 18.75 cc. of 0.1 N as the total acid in 100 cc. of distillate. In this there is

$I = 0.28 \times Q_{100} = 5.250$ cc. of acetic
$i = 0.12 \times Q_{100} = 2.250$ cc. of propionic
$m = 0.60 \times Q_{100} = 11.250$ cc. of butyric
$Q_{100} =$ **18.75** cc. of 0.1 N (other acids than formic)

$I/0.7784 = 1.285$ acetic acid in the original 110 cc., since 77.81. is the percentage of acetic acid coming over in 100 cc. of distillate (Table I).

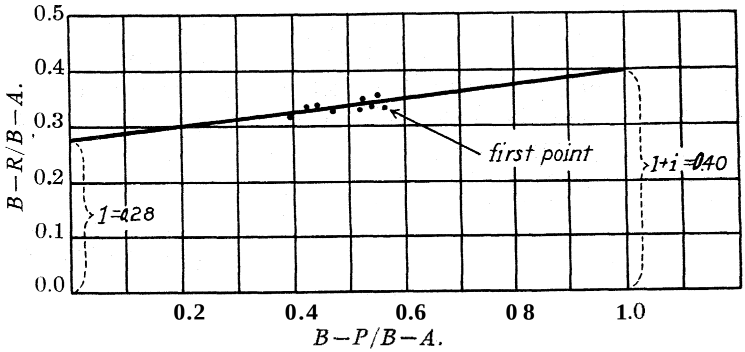

Fig. 1.

$I/0.9508 = 1.052$ propionic acid in the original 110 cc., since 95.08 is the percentage of propionic acid coming over in 100 cc. of distillate (Table I). $I/0.9774 = 1.023$ butyric acid in the original 110 cc., since 97.74 is the percentage of butyric acid coming over in 100 cc. of distillate (Table I).

	Found, cc. of 0.1 N	Present, cc. of 0.1 N	Error, cc. of 0.1 N
$x = 1.285 \times 5.25 =$	6.75 acetic	5.35	+1.40
$y = 1.052 \times 2.25 =$	2.37 prop.	4.90	−2.53
$z = 1.023 \times 11.25 =$	11.51 butyr.	9.98	+1.63
	7.38[5] formic	7.91	−0.53[5]
Total	28.01	28 04	−0.03

Better accuracy could have been attained by taking special precautions with the technique throughout. The above, however, serves to illustrate the new procedure. Details as to the method and calculations may be found in Gillespie and Walters' paper referred to above, to the senior author of which the present writer desires to acknowledge assistance with the calculations involved.

The results of the analyses of high and low percentage mixtures of formic, acetic, propionic and butyric acids are shown in Table IV.

Use of the Duclaux Method for Unknown Mixtures.—When more than four acids are present in significant quantities, more than one acid must be

(5) This should be 7.83 and the error should be therefore 0.08 cc.

determined chemically or the solution must be fractionated into mixtures containing only four acids in significant quantities before applying the Duclaux method. If necessary, the acids may be freed partially from their salts and distilled, as suggested by Liebig[6] and Gillespie and Walters.[1]

To use the Duclaux method most successfully, the acids met with should be identified qualitatively before calculating the results. The tests suggested by Agulhon and rearrangement by Dyer seem the most practicable. These tests depend upon the relative solubility of the iron and copper salts of the fatty acids in various organic solvents.[7]

Summary

A new procedure has been outlined, illustrated by an example, for the estimation of four acids by the Duclaux method. In the new procedure one or more acids are determined quantitatively by chemical methods and the remainder determined by the Duclaux method.

[6] Liebig, *Ann.*, **71**, 355 (1849).

[7] J. *Biol. Chem.*, 28, 445–473 (1917).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Conductivity of Grignard Reagents in Ether Solutions

BY W. V. EVANS AND F. H. LEE

The conductivity of the Grignard reagent in ether solutions has been studied by numerous investigators. Kondyrew and Manojew[1] measured the conductivity of ethylmagnesium bromide at various temperatures. Kondyrew and Ssusi[2] studied the effect of dilution on the conductivity of ethylmagnesium iodide and postulated the formation of complex organic compounds at certain concentrations. Recently Dufford and his co-workers[3] investigated the effect of light on the conductivity of these solutions. In the present work we have extended this investigation to several other Grignard compounds.

Experimental

Preparation of Solutions.—Pure dry alkyl or aryl bromide was mixed with ether and added to dry magnesium turnings in slight excess of the amount necessary for the reaction $RX + Mg = RMgX$. After reaction the flask was heated for two hours on a water-bath. All precautions were taken against the entrance of air and moisture.

Measurement of Conductivity.—The conductivities of ethylmagnesium bromide, benzylmagnesium bromide, n-butylmagnesium bromide, phenylmagnesium bromide, and magnesium bromide have been measured at 20, 0 and −10°. The solubility of magnesium bromide in ether is so small that only the conductivity of dilute solutions of

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[1] Kondyrew and Manojew, *Ber.*, 68, 464 (1925).

[2] Kondyrew and Ssusi, *ibid.*, 62, 1856 (1929).

[3] Dufford, Phys. *Rev.*, **35**, 998 (1930); *J. Phys. Chem*, *34*, 1544 (1930).

this salt could be obtained. Solutions half saturated at 22" were used in the conductivity measurements. From the specific conductivity of this solution of magnesium bromide a very rough approximation of the specific conductivity of a molar solution can be made. The results are given in Table I.

TABLE I

SPECIFIC CONDUCTIVITY OF *M* GRIGNARD REAGENTS

Temp., °C.	C_2H_5MgBr	$C_6H_5CH_2MgBr$	n-C_3H_7MgBr	C_6H_5MgBr	$MgBr_2$(0.0705M)
20	6.25×10^{-5}	5.55×10^{-5}	4.75×10^{-5}	4.40×10^{-5}	0.137×10^{-5}
	6.08×10^{-5}	6.08×10^{-5}	4.50×10^{-5}	5.00×10^{-5}	
	6.14×10^{-5}	6.00×10^{-5}	4.71×10^{-5}	4.83×10^{-5}	
	6.16×10^{-5}	5.88×10^{-5}	4.65×10^{-5}	4.74×10^{-5}	(1.93×10^{-5})[a]
0	8.95×10^{-5}	7.48×10^{-5}	8.03×10^{-5}	4.86×10^{-5}	0.180×10^{-5}
	10.53×10^{-5}	8.38×10^{-5}	7.70×10^{-5}	5.38×10^{-5}	
	10.23×10^{-5}	8.00×10^{-5}	8.00×10^{-5}	5.35×10^{-5}	
	9.90×10^{-5}	7.95×10^{-5}	7.91×10^{-5}	5.20×10^{-5}	(2.55×10^{-5})[a]
−10	13.95×10^{-5}	8.46×10^{-5}	11.00×10^{-5}	6.17×10^{-5}	0.296×10^{-5}
		8.09×10^{-5}	11.80×10^{-5}		
		8.28×10^{-5}	11.40×10^{-5}		(4.16×10^{-5})[a]

[a] Specific conductance of *M* $MgBr_2$ calculated.

Order of Conductivity.—It is observed from Table I that the order of the conductivities at any given temperature seems to be ethyl-, n-butyl-, benzyl- and phenyl- with magnesium bromide showing the least conductivity. The calculated specific conductivity of a molar solution of magnesium bromide is about one-third the conductivity of a molar solution of ethylmagnesium bromide. We also observe that in all cases between the limits of 20 and −10" the conductivity of ethylmagnesium bromide is of the order of twice the value for phenylmagnesium bromide. Benzyl- and n-butyl-, however, seem to have approximately the same conductivity. We would, therefore, reach the conclusion that ethylmagnesium bromide is the more highly ionized. In order to test this conductivity further, measurements were made on 2 M and 0.5 M solutions of ethylmagnesium bromide and phenylmagnesium bromide. The results are shown in Tables II and III.

Temperature Coefficient

Table I shows very definitely that all of these compounds have negative temperature coefficients between 20 and −10°. Ethylmagnesium bromide, for instance, has more than twice the conductivity at −10° that it has at 20°. Benzylmagnesium bromide and phenylmagnesium bromide also increase but the increase is not so striking. We also note from Tables II and III that the 0.5 M solutions of ethylmagnesium bromide and

TABLE II

SPECIFIC AND MOLAR CONDUCTIVITY OF ETHYLMAGNESIUM BROMIDE[a]

Temp., °C.	2 Molar		1 Molar		1/2 molar	
	L	μ	L	P	L	P
20	18.3×10^{-5}	9.2×10^{-2}	6.14×10^{-5}	6.14×10^{-2}	1.62×10^{-5}	3.24×10^{-2}
0	21.8×10^{-5}	10.9×10^{-2}	9.95×10^{-5}	9.95×10^{-2}	3.99×10^{-5}	7.98×10^{-2}
−10	24.4×10^{-5}	12.2×10^{-2}	13.80×10^{-5}	13.80×10^{-2}	5.65×10^{-5}	10.30×10^{-2}

TABLE III

SPECIFIC AND MOLAR CONDUCTIVITY OF PHENYLMAGNESIUM BROMIDE[a]

Temp., °C.	2 Molar		1 Molar		1/2 Molar	
	L	μ	L	μ	L	μ
20	10.07×10^{-5}	5.04×10^{-2}	4.83×10^{-5}	4.83×10^{-2}	1.21×10^{-5}	2.42×10^{-2}
0	8.24×10^{-5}	4.12×10^{-2}	5.35×10^{-5}	5.35×10^{-2}	1.94×10^{-5}	3.88×10^{-2}
−10	7.50×10^{-5}	3.75×10^{-2}	6.17×10^{-5}	6.17×10^{-2}	2.64×10^{-5}	5.28×10^{-2}

[a] We realize that these solutions do not contain the theoretical amount of Grignard compound since a considerable quantity of magnesium halide is always formed. However, we have discovered that the conductivity of this compound is slight compared to the conductivity of the complex compound in equilibrium with the simple Grignard reagent. Furthermore, we were determining the relative conduction of Grignard solutions as they exist.

phenylmagnesium bromide have negative temperature coefficients. The conductivity of 2 M ethylmagnesium bromide, however, does not increase so markedly with decreased temperature and 2 M phenylmagnesium bromide has less conductivity at −10° than at 20°, and hence at some concentration between 2 M and 1 M the temperature coefficient changes its sign. This same change in conductivity with temperature would no doubt take place with ethylmagnesium bromide. In fact, Kondyrew[1] found that 2.3 N ethylmagnesium bromide had a positive temperature coefficient and at 1.4 and 0.7 N the coefficient had a negative value.

Effect of Dilution on Molar Conductivity.—Our results show that the molar conductivity decreases with dilution between 2 M and 0.5 M. This is just the opposite of the effect we would expect if this weak electrolyte was obeying classical dilution laws. These results are not in accord with Kondyrew's results for ethylmagnesium bromide owing to the fact that he was working with more concentrated solutions in most cases. They do, however, check his results for ethylmagnesium iodide where he finds conduction to increase with concentration to 4 N and then decrease. Facts such as are tabulated here can be explained by postulating a complex structure to the Grignard reagent such that in dilute solutions the ionization decreases with dilution. We are at present investigating this phenomenon by determining the migration rates of the ions and identifying the products of electrolysis.

Summary

1. The conductivities of ethylmagnesium bromide, benzylmagnesium bromide, n-butylmagnesium bromide and magnesium bromide have been determined at 20, 0 and −10° and at various concentrations.

2. The conductivity of the ethylmagnesium bromide solution is the greatest. The order of conductivity is ethylmagnesium bromide, *n*-butylmagnesium bromide, benzylmagnesium bromide, phenylmagnesium bromide, and magnesium bromide.

3. The conductivity in all cases except 2 M phenylmagnesium bromide increases with decreased temperature.

4. Molar conductivity of ethylmagnesium bromide decreases with dilution.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Extractability of Vitamins B and G by Plain and Acidified Alcohol

BY H. K. STIEBELING AND I. L. ALLEMAN

Introduction

By adding gallic or tannic acid to the alcohol used in extracting wheat germ, McCollum and Kruse[1] obtained a more potent extract of water-soluble B than by the use of plain alcohol. They interpreted their results to indicate that the solubility of the salt of the vitamin was greater than that of the vitamin itself, or that the molecular structure of these acids favored the formation of the salt.

Water-soluble B has since been shown to comprise at least two factors, the antineuritic vitamin B, and the more heat-stable vitamin G. Since reviews of the literature have so recently been published by Kruse and McCollum[2] and by Sherman and Smith,[3] a review of the solubility of the vitamins in alcohol is not included here. In general, both vitamins B and G are soluble in alcohol. Vitamin B appears to be soluble in ethyl alcohol of all concentrations, and vitamin G in the more aqueous solutions. However, Sherman and Sandels[4] have found it necessary to consider the physical and chemical nature of the source material as well as the solvent and the method of extraction in evaluating the evidence regarding the solubilities (extractabilities) of vitamins. This paper reports the relative extractabilities of the two vitamins by plain and acidified alcohols from the same source material and under the identical extraction procedures. The original source material and the extracts and residues resulting from the alcoholic extraction were assayed for each of the vitamins.

(1) McCollum and Kruse, Am. J. *Hyg.*, **6**, 197 (1926).

(2) Kruse and McCollum, *Physiol. Rev.*, 9, 125 (1929).

(3) Sherman and Smith, "The Vitamins," Am. Chem. Soc. Monograph (1931).

(4) Sherman and Sandels, *Proc. Soc. Expll. Biol. Med.*, **26**, 536 (1929); J. *Nutrition*. **3**, 395 (1931).

Materials and Methods Used

Skim milk powder was chosen as the source material in this study since it contains both vitamin B and vitamin G, and is relatively richer in vitamin G, regarding which the less was known. A composite sample of the milk powder was used throughout the investigation.

Ethyl alcohol 80% by weight was selected as solvent. Both vitamins were known to be soluble in plain alcohol of this strength, but not completely extracted from skim milk powder by it. To study the effect of acidification of the alcohol upon the extractability of the vitamins, the alcohol was used plain and **0.1** M with respect to gallic, benzoic and hydrochloric acids. These acids were selected, primarily because of their variety in structure, but also because of the varying hydrogen-ion activity in **0.1** M concentrations.

The method of extracting the milk powder with the alcohols was as follows. To **200** g. of skim milk powder was added **500** cc. of purified ethyl alcohol, **80%** by weight, plain, or **0.1** M with respect to gallic, benzoic or hydrochloric acid. The mixture was thoroughly stirred, allowed to stand at room temperature (**20** to 25°) for one hour, stirred and allowed to stand for a second hour. The supernatant fluid was then decanted and filtered, and to the residue was then added **500 cc**. of fresh plain or acidified alcohol; the mixture was stirred and allowed to stand for an hour, stirred again, and allowed to stand for a second hour, after which the solution was decanted and filtered, and the residue washed twice by decantation, each time with **200** cc. of the alcohol. The filtrates and washings of both extractions were combined and concentrated to about one-fourth of the original volume by distillation under reduced pressure (temperature about **30°**). The concentrated filtrates and the residues were dried separately in evacuated desiccators over sulfuric acid, and were then ground to a fine powder. Identical products were tested in parallel for each of the two vitamins under consideration.

In principle and in most of the details, the methods used for testing the potency of these products in vitamins B and G and thus determining the relative extractability of the vitamins were those described by Chase and Sherman and by Bourquin and Sherman.[5]

Results

The results of this investigation are summarized in Table I.

TABLE I

RELATIVE EXTRACTABILITY OF VITAMINS B AND G BY PLAIN AND ACIDLFIED ALCOHOLS

	Vitamin B		Vitamin G	
	Units	Percentage	Units[b]	Percentage
Source material (skim milk powder), **100** g.	**130**	**100**	**500**	**100**
Products resulting from treating **100** g. source material with:				
Plain alcohol				
Extract	75	**60**	**50**	**10**
Residue	**50**	**40**	**175**	**35**
Total recovered	**125**	**100**	**225**	**45**
Alcohol, **0.1** M with respect to benzoic acid				
Extract	55	40	50	10
Residue	45	35	175	35
Total recovered	100	75	225	45

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[5] **Chase and Sherman, THIS JOURNAL, 53, 3506 (1931); Bourquin and Sherman, *ibid.*, 63, 3501 (1931).**

TABLE I (*Concluded*)

	Vitamin B		Vitamin G	
	Units[a]	Percentage	Units[b]	Percentage
Alcohol, 0.1 M with respect to galiic acid				
Extract	60	45	150	30
Residue	50	40	175	36
Total recovered	110	85	325	65
Alcohol, 0 1 M with respect to hydrochloric acid				
Extract	60	45	26	5
Residue	50	40	175	35
Total recovered	110	85	200	40

[a] As defined by Chase and Sherman. [b] As defined by Bourquin and Sherman.

Under the conditions of fractionation here employed, between 35 and 40% of vitamin B was left in the residual matter, whether the alcohol used in the extraction was neutral or acidified. The extracts were somewhat richer in the vitamin than the corresponding residues from the same quantity of source material and were found to contain about half of the vitamin B of the original material. From three-fourths to practically all of the vitamin B of the source material was recovered either in the residues or in the extracts. The apparent loss of vitamin B during the fractionation was greatest in the case of the products prepared by means of alcohol acidified with benzoic acid. This apparent loss may perhaps be attributed to a destruction of the vitamin B by the benzoic acid or to the limitations of the biological method of assay.

About one-third of the vitamin G of the source material was found to be left in the residual matter. With this vitamin as with vitamin B, acidulation of the alcohol had no apparent effect upon extractability. Perhaps these negative results may be due in part to the protein nature of the source material. However, in addition to their reaction with the protein certain acids when added to the alcohol used in the extraction did markedly influence the stability of the extracted vitamin G. The extract prepared by the use of alcohol acidulated with hydrochloric acid contained practically no vitamin G whereas that prepared by the use of alcohol acidulated with gallic acid contained approximately 30% of the vitamin G of the source material. In no case were the extracts as potent in this vitamin as the corresponding residual matter.

Large losses of vitamin G were encountered in every fractionation--over 50% in every case except when the alcohol used in the extraction was acidulated with gallic acid. The least loss was encountered when gallic acid was added to the alcohol; the greatest, when hydrochloric acid was added. The high concentration of vitamin G found in the extract made by the use of alcohol acidified with gallic acid, a phenomenon also observed by McCollum and Kruse for the vitamin B complex, is not due to the greater solubility of the vitamin or its salt as suggested by those workers, since the increase in concentration of the vitamin in the extract was not accompanied by a decrease in the corresponding residual matter. Apparently the higher concentration is due to a conserving action which the gallic acid has on the vitamin in alcoholic solution and which is related perhaps to the higher reduction potential of the gallic acid present.

Bisbey[6] found that losses of vitamin G in strong alcoholic solution can be considerably diminished by working as nearly as practicable under an atmosphere of nitrogen. Chick and Roscoe and Narayanan and Drummond[7] have also observed inactivation of vitamin G in alcoholic solution. In the investigation here described, the loss of vitamin G in the extracts is probably attributable in part to oxidation catalyzed both by acid and by alcohol.

Summary

1. Under the conditions of fractionation described, about half of the vitamin B of the source material was recovered in the extracts. The vitamin G content of the extracts varied widely, however. The extract prepared by means of alcohol acidified with gallic acid contained about 30% of the vitamin G of the original material; that prepared by means of alcohol acidified with hydrochloric acid contained practically none.

2. Approximately the same proportions of vitamin B and G, from one-third to two-fifths, were left in the residual matter. Acidifying the alcohol with benzoic, gallic or hydrochloric acid did not increase the extractability of either vitamin.

3. Large losses of vitamin G were met in each fractionation but the addition of gallic acid to the alcohol used in the extraction appeared to conserve the vitamin G of the extract.

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(6) Bisbey, Dissertation, Columbia University, 1930.

(7) Chick and Roscoe, Biochem. J., 23, 504 (1929); Narayanan and Drummond, *ibid.*, 24, 19 (1930).

[FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Potentiometric Studies on Semiquinones

BY LEONOR MICHAELIS AND EDGAR S. HILL

I. General and Theoretical Part

There are numerous aromatic compounds on an oxidation level intermediary between a quinone and hydroquinone, or between a diamine and a diimine, or between phenazine and dihydrophenazine, and comparable instances. The cases of a-oxymethylphenazine (pyocyanine),[1a] of α-oxyphenazine[1b,1c,1d] and of Wurster's dyes[1e] have been discussed in previous papers. A potentiometric study showed that the intermediary compounds are radicals with an odd number of electrons and of the same molecular size as the fully oxidized or the fully reduced form, and not bimolecular meriquinones such as suggested by Willstatter and Piccard.[2] Our assumption is in agreement with Weitz,[3] who, in special cases, succeeded in determining the molecular weight by the boiling point method. In contrast herewith, our method was a potentiometric one.

Certain difficulties in the application and interpretation of the potentiometric method had to be overcome to arrive at these results. In the first place, the substances concerned may be, in one form or other of the three levels of oxidation, difficult to dissolve. This prevents the establishment of a homogeneous system during the oxidative or reductive titration and makes the interpretation of the titration curve difficult. An instance of this kind is phenazine, of which a green intermediary state of reduction has been known for a very long time. This difficulty can be overcome by applying an organic solvent, especially acetic acid. Another difficulty may arise from the fact that sometimes one of the three forms is an unstable molecule undergoing a rapid and irreversible rearrangement or destruction. In some cases, the intermediary form is the most unstable one, *e. g.*, in the benzidine compounds. Sometimes the completely oxidized form is the most unstable, *e.* g., in Wurster's dyes. In some cases the completely reduced form is the unstable one, namely, in γ,γ'-dipyridyl.

None of the cases to be described in this paper shows any evidence that the radical might undergo a partial polymerization, in the way triphenylmethyl partially associates to hexaphenylethane. The explanation may be found in the fact that all these semiquinones have the character of cations and very likely do not exist at all or have only a very short lifetime in an un-ionized condition. It is, however, unlikely that two molecules of a

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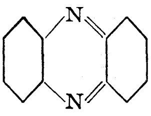
(1) (a) Friedheim and Michaelis, *J.* Biol. Chem , 91, 355 (1931); see also Elema, *Rec. trav chim. Pays-Bas*, 60, 807 (1931). (b) Michaelis, J. *Biol* Chem., 92, 211 (1931). (c) Michaelis, *ibid.*, 96, 703 (1931). (d) Michaelis, Hill and Schubert, *Biochem.* Z., 255, 66 (1932). (e) Michaelis, THIS JOURNAL, 53, 2953 (1931).

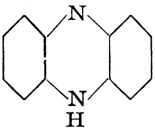
(2) Willstatter and Piccard, *Ber.*, 41, 1458 (1908).

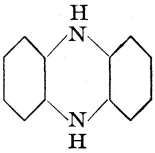
(3) (a) Weitz, *Z.* Elekfrochemie, 34, 538 (1928); (b) Weitz, Konig and Wistinghausen, Rer , 57, 153 (1924); (c) Weitz and Fischer, ibid., 59, 432 (1926).

univalent cation should combine to any appreciable extent to form one molecule of a bivalent cation, for electrostatic reasons. In contrast herewith, in the case of triphenylmethyl or diphenyl nitride, two electroneutral molecules associate to form a double molecule.

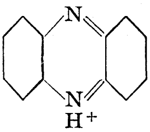
To illustrate the matter, let us consider what takes place with phenazine. Disregarding all ionizations, we may write the three forms in this way

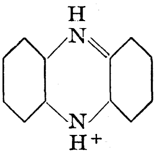

I

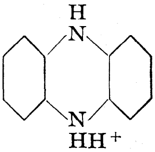

II


III

I is the oxidized form of phenazine, II the intermediary form, which in the language of these formulas contains a "bivalent" nitrogen atom, and III is the completely reduced form. Experience, however, shows that II is obtainable only in acid solutions. On writing these formulas as they occur in moderately acid solutions, as univalent cations, we obtain

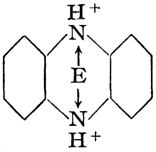

Ia


IIa


IIIa

In order to explain the existence of a molecule such as IIa we rewrite it in the following way

IIb



Here E means an electron. We assume that this electron has no definite place in one N-atom but is shared by both N-atoms. The outer electron shell of each nitrogen atom is a septet, and one odd electron alternatively fills up the one or the other septet to an octet. Each N-atom with a septet may be very unstable and liable to secondary, possibly irreversible, reactions. Nevertheless, its life-time will have some short duration (there are even cases known in which the septet is a fairly stable arrangement, as in triphenylmethyl and biphenyl nitride). Before any irreversible disruption happens to the whole structure, the septet is filled up again to form an octet. Thus the oscillation of the odd electron between the two septets imparts to the whole structure sufficient stability, even where the septet structure, without the support of the oscillating eighth electron, might be a more labile structure.

One way of picturing the status of the odd electron is to assume that this electron has a path around both N-atoms jointly. In this way, the situation was tentatively pictured in the previous paper.[1e] It seems advisable not to take this picture too literally. Mechanical models for atomic structures involving definite circuits of electrons have been abandoned by atom physicists. Suffice it to express the situation by saying that the probability of the odd electron being a constituent of the one nitrogen atom or the other is the same. At any rate this configuration is equivalent to an electric oscillator and can be considered responsible for the very intense coloring of these compounds.

The molecule of formula IIa or IIb is a univalent cation. In no other state of dissociation can the regular periodic oscillation be imagined. If this oscillation be the principle maintaining the structure of the otherwise labile molecule, the monovalent cation should be more stable than all the other forms of dissociation. In fact, all these semiquinones are stable only in moderately acid solutions; and in the case of the aromatic diamines it will be shown in the special part that the lability is very considerably increased when, by changes in PH, the state of ionization is altered.

The idea suggests itself to correlate the hypothesis of the alternating odd electron of the semiquinone-like molecules with the very distinct and beautiful band spectrum exhibited by the majority of these compounds (namely, all alkylated aromatic diamines, and the derivatives of γ,γ'-dipyridyl) in their semiquinoid form. This is even more so as another group of radicals with an odd electron exhibits the same type of band spectrum, such as triphenylmethyl and related compounds.[4] It fits the hypothesis presented very well, that the very distinct band spectrum is shown, in the case of triphenylmethyl, by the electroneutral radical, whereas in the case of Wurster's dyes or the half-reduced dipyridyl compounds, the band spectrum is encountered in the form of the univalent cations.

II. Special and Experimental Part

1. Materials Used.—Dimethyl-, tetramethyl-, diethyl- and tetraethyl-*p*-phenylenediamine were used in the form of the commercial hydrochlorides (Eastman), the two first mentioned after recrystallization according to previous directions[1*] without changing the results.

Diphenyl-p-phenylenediamine was prepared according to v. Bandrowski[S] and Calm,[6] by what the first of these authors calls his third method.

γ,y-Dipyridyl was prepared in the following way. Diacetyl-[tetrahydro-y,γ'-dipyridyl] was prepared according to Dimroth and Heene.[7] This substance on suitable oxidation directly yields γ,γ'-dipyridyl. This oxidation is a somewhat variable reaction, the yields differing widely. Dimroth and Heene recommend the bubbling of oxygen

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(4) Meyer and Wieland, *Ber.*, 44, 2557 (1911).

(5) V. Bandrowski, Monatsh., 8, 475 (1887).

(6) Calm, Ber., 16, 2786 (1883); cf. p. 2805

(7) Dimroth and Heene, *ibid.*, **54**, 2934 (1921).

through the suspension of the above substance. We found the following method most convenient. The freshly prepared substance was exposed to the air at 48° in an open dish for two or three days until it had been converted into dark brown lumps with a strong smell of acetic acid. Ten grams of these lumps was suspended in 300 cc. of water and ten grams of manganese dioxide added and the mixture shaken at room temperature for half an hour. Then enough saturated solution of disodium phosphate is added to bring the acid reaction almost to neutrality. The liquid is now filtered off. It is yellow-brown in color. By adding a suitable amount of sodium hydroxide the γ,γ'-dipyridyl directly crystallizes in white, shiny needles. The yield is far from the theoretical but satisfactory for the preparation.

N,N'-Dimethyl-γ,γ'-dipyridylium chloride was prepared in the following way. Five-tenths gram of γ,γ'-dipyridyl is heated in a test-tube with 3 cc. of dimethyl sulfate for a short time until the crystals are completely dissolved. This solution is poured into 30 cc. of water, the excess of dimethyl sulfate removed by washing with ether, enough aqueous solution of picric acid is added to bring about a complete precipitation of the picrate. The crystals are collected on a Buchner filter, washed with picric acid solution and shortly with water, then dried. After grinding, they are suspended in a rather strong hydrochloric acid solution. For each gram of the picrate 40 cc. of concentrated hydrochloric acid plus 160 cc. of water is an appropriate amount. This suspension is heated to complete solution, and while still warm, before recrystallization starts, is extracted with toluene. This extraction is repeated later on with ether, to the complete removal of the picric acid. The colorless solution is evaporated to dryness, either on a steam-bath, or in *vacuo* at 50°, the dry residue dissolved in methyl alcohol. Then benzene is added. This solution is heated on the steam-bath until enough methyl alcohol has been removed to allow a separation of the chloride of the base. The crystals are filtered off, washed with benzene, dried and redissolved in ethyl alcohol. On addition of a suitable amount of benzene, crystallization begins. In the ice box beautiful, long, shiny, colorless needles are formed and can be collected on a filter. Five-tenths gram of r,?'-dipyridyl gave 0.53 g. of the dry chloride of the ammonium base, or 65% of the theoretical yield.

The analysis gave the following results (Dr. Elek): C, 55.11; H, 5.70; N, 11.07; Cl, 26.59. Calcd. for $C_{12}H_{14}N_2Cl_2$: C, 56.25; H, 5.47; N, 10.94; Cl, 27.34.

Benzidine, o-tolidine, tetramethylbenzidine were commercial preparations, recrystallized. Tetrabromobenzidine and dibromotolidine were prepared according to Schlenk.[8]

Phenazine was prepared in the following way, which is rather obvious, though we could find no reference to just this modification probably because of the small yield procurable by the method.

Two grams of pyrocatechol is dissolved in 250 cc. of dry ether. Twenty grams of dry lead peroxide is added. After shaking for thirty minutes the lead peroxide is removed by filtering and washed out with some more ether. The red-brown filtrate is mixed with a solution of 2 g. of o-phenylenediamine in a mixture of glacial acetic acid and ether. After an hour this ether solution is extracted successively once with 2% hydrochloric acid, twice with 5% sodium hydroxide and with water. The remaining ether is amber-yellow. The ether is evaporated and the residue sublimed in *vacuo*. After one sublimation the sample melted at 171°. Nitrogen, 15.46; calcd., 15.55%.

Methoxyphenazine was prepared according to Wrede and Strack[9] with a slight modification especially in the preparation of the asymmetrical pyrogallol monomethyl ether, which is requisite for the synthesis, as described in a previous paper.[1e]

A series of various naphthazonium compounds was placed at our disposal by Dr. W. A. Jacobs. Thanks are due to him.

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(8) Schlenk, *Ann* , 363, 313 (1908)

(9) Wrede and Strack, *Z. physiol Chem* , 181, 58 (1929); Aer , 62,2051 (1929).

The methods of titration are the same as described in previous papers.[10] All titrations were performed in a stream of nitrogen purified by heated copper.''

Special Part

1. The Alkylated Aromatic **Diamines.**—In *p*-phenylenediamine the first step of oxidation is too labile a compound to be worthy of a careful study On oxidation with bromine or any other strong oxidant it turns successively to light yellow, green, red, colorless. The first yellow product is probably the semiquinone, but the potentials drift too much for any reliable information. Piccard[12] considers the green stage as what he called the meriquinone. It is possible that he did not give attention to the first yellow stage which is obtained by adding a very small amount of oxidant to a large excess of the diamine in the P_H range of the acetate buffer.

In asymmetrical dimethyl-p-phenylenediamine, the substance produced in the first stage of the oxidation, Wurster's red, is much more stable, and in tetramethyl-*p*-phenylenediamine it is a perfectly stable substance (Wurster's blue). In pres- of an excess of the unoxidized diamine, the potentials are perfectly stable. Otherwise even with the tetramethyl compound, a drift of the potential occurs due to the fact that the second step of oxidation, the tetramethyl-diimonium compound, is extremely labile. Stable and interpretable potential readings can be obtained, therefore, only up to about 60–70% of

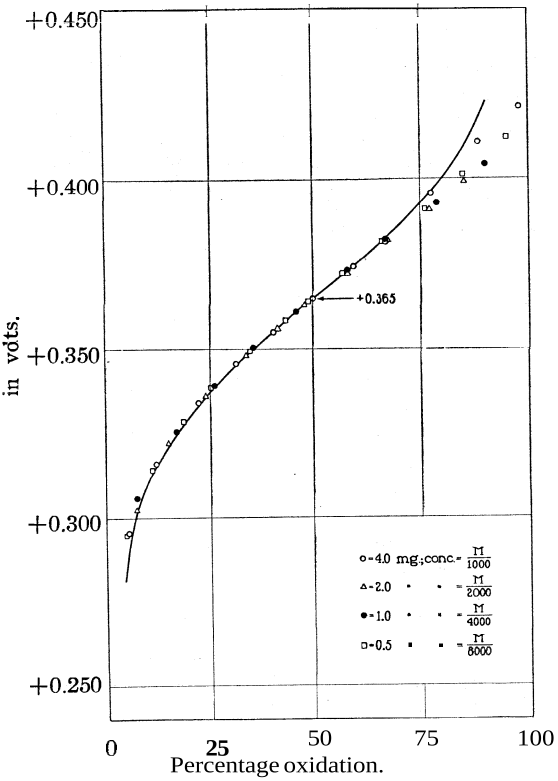

Fig. 1.—Independence of the normal potentials of tetramethyl-*p*-phenylenediamine on the initial concentration: potentials are plotted against percentage of oxidation; ordinate is potential in volts; abscissa is percentage of oxidation; potentials referred to the normal hydrogen electrode; P_H 4.620, varying no more than ±0.01 in the individual titration experiments.

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(10) Michaelis and Eagle, J. *Biol. Chem.*, 87, 713 (1930)

(11) Michaelis and Flexner, ibid., 79, 689 (1928).

(12) Piccard, *Ber*, 46, 1843 (1913).

the theoretical end-point of the titration of the first step. Therefore, in the previous paper only the first half of the curves was used to calculate the results. It is desirable, however, to prove that the neglect of the second half of the curve, with drifting potentials, is justified. Such proof can be given by showing that a number of consequences ensuing from our interpretation can be corroborated by independent methods. There are three corollaries of our interpretation: (a) if our hypothesis is correct, the potential, as plotted against percentage of oxidation, should be independent of the initial concentration of the substances. In part this has been shown in the previous paper.[1e] It can, however, be shown to a much greater extent by the following experiments (see Fig. 1).

(b) If the hypothesis is correct, the amount of a mono-equivalent oxidant used up at the supposedly 50% point of the titration should be half the molar amount of the initial diamine. This is proved by the data shown in Table I.

TABLE I[a]

5.17×10^{-5} MOLE OF DIMETHYL-*p*-PHENYLENEDIAMINE HYDROCHLORIDE DISSOLVED IN 20 CC. OF ACETATE BUFFER, PH 4.62, AND TITRATED WITH BROMINE, THE WHOLE TITRATION LASTING ABOUT THREE MINUTES

E calculated according to the formula $E = 0.447 + 0.0601 \log \%\ \text{oxidation}/100 - \%\ \text{oxidation}$.

Br_2 soln., cc.	% Oxidation, to the first step	*E* in volt Obs.	*E* in volt Calcd.
0.0	0.0		
.250	10.8	+0.394	+0.392
.641	27.6	.424	.422
.988	42.5	.440	.439
1.398	60.2	456	.457
1.780	76.7	470	.478
2 082	89.7	.478	.503

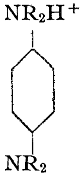
By titration, 10 cc. of the bromine solution after adding an excess of potassium iodide, used up 2.255 cc. of *N*/10 sodium thiosulfate. At the midpoint (50% oxidation), 1.16 cc. bromine had been used up according to graphic interpolation.

$1.16 \times 2.255 \times 10^{-5} = 2.61 \times 10^{-5}$ gram atom of bromine used for one-half of the first step of oxidation and = one-half the initial concentration of the diamine (2.59×10^{-5}).

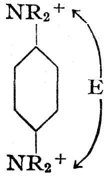
[a] All potentials in this paper are referred to the normal hydrogen electrode. They were measured against a saturated calomel half cell the potential of which was frequently checked by comparison with the hydrogen electrode in standard acetate buffer the *P*H of which was taken as 4.620. The temperature was always 30 ± 0.1° and maintained by working in a constant temperature room.

(c) If the hypothesis is correct, a series of titration curves over a wide range of PH would enable us to draw a plot showing the normal potential as a function of PH. The slope of this curve should be constant as long as no change of the dissociation interferes. Considering the state of ionization in moderately acid solution, we have to assume the primary cation (formula A) for the diamine, where R is alkyl or hydrogen, and the formula

B for the oxidized form. These two molecules differ by one hydrogen atom, hence the slope of our curves should be 0.06 volt per P_H unit in moderately acid solutions. This is true, as Fig. 2 shows. It is obvious that this slope cannot be maintained throughout all ranges of P_H. In fact, the diagram (Fig. 2) shows bendings of the slope at either end of the curves. Where these bendings begin, the potentials become so strongly drifting that accurate determinations of the normal potentials become difficult or even impossible. The change of the slope indicates that the substances change their state of dissociation. It fits very well the theory presented, that simultaneously with the change of dissociation the stability of the substances is lost. The arrows in Fig. 2 show the dissociation exponents of the diamines (in their original, reduced form) as directly determined by acidimetric titration with the hydrogen gas electrode. They agree fairly well with the bends of the curves considering the limits of error in those P_H ranges where the potential drift becomes disturbing. Tables II, III, and IV are records of representative individual titration experiments, included to show the agreement between our observed potential values and those calculated according to the theory. The agree-



A



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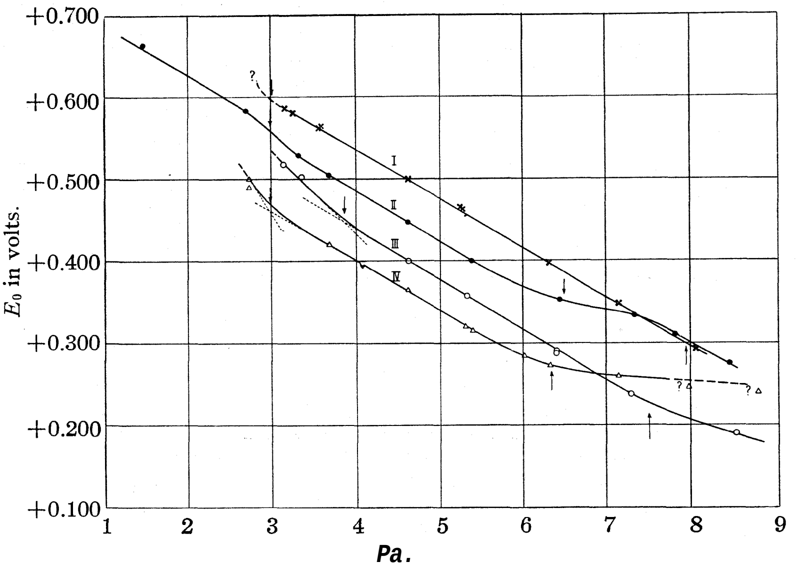

Fig. 2.—Normal potentials are plotted against P_H for the four alkylated diamines as follows: x, diethyl-p-phenylenediamine; ●, dimethylphenylenediamine; O, tetraethylphenylenediamine; A, tetramethylphenylenediamine; ordinates, normal potential in volts; abscissas, P_H; potentials referred to the normal hydrogen electrode.

ment is in general much better for the tetramethyl compound because there is practically no drift of the potential up to about 60% of the oxidation. This statement is in an unexplainable contradiction to the one of Clark, Cohen and Gibbs,[13] who report stronger drifts for the tetramethyl than for the dimethyl compound.

TABLE II

TETRAMETHYL-*p*-PHENYLENEDIAMINE

Oxidant, bromine. P_H, 3.657 (acetate buffer). Concn. = 2 mg./20 cc. = *M*/2000. E = 0.420 + 0.0601 log % oxidation/ (100 − % oxidation)

% oxidation	Observed potential	Calculated potential
4.09	+0.3420	+0.3381
10.0	.3639	.3632
15.3	.3766	.3760
23.1	.3894	.3889
30.4	.3995	.3991
37.6	.4075	.4072
44.5	.4151	.4149
53.06	.4229	.4231
60.2	.4293	.4317
70.1	.4379	.4422
78.2	.4442	.4532

The agreement of the observed and calculated values is satisfactory up to 53% of oxidation.

TABLE III

TETRAMETHYL-p-PHENYLENEDIAMINE

Oxidant, bromine. P_H, 4.628 (acetate buffer). Concn. = 0.5 mg./20 cc. = *M*/8000. E = 0.365 + 0.0601 log % oxidation/(100 − % oxidation)

% oxidation	Observed potential	Calculated potential
11.2	+0.3143	+0.3130
18.2	.3283	3261
25.7	.3387	.3380
34.5	.3492	.3483
43.2	.3580	.3579
48.8	.3639	.3638
57.7	.3725	.3731
66.7	.3812	.3831
76.3	.3909	.3954
85.2	.4010	.4100
94.6	.4120	.4390

Agreement between observed and calculated values is satisfactory up to about 60% of oxidation.

TABLE IV

DIMETHYL-p-PHENYLENEDIAMINE

Oxidant, bromine. P_H, 4.620 (acetate buffer). Concn. = 2 mg./20 cc. = *M*/1725 E = 0.450 + 0.0601 log % oxidation/(100 − % oxidation)

% oxidation	Observed potential	Calcd. potential
8.26	+0.3886	+0.3873
19.2	.4140	.4126
40.3	.4409	.4402
52.3	.4520	.4523
71.5	.4710	.4739
88.8	.4877	.5039

Note to Tables II to IV.—Duration of the whole titration experiment for the dimethyl compound two to three minutes. For the tetramethyl compound the duration of the experiment is irrelevant up to 60% of oxidation.

2. Phenylated **Diamines.**—The diimines of the phenylated aromatic diamines, in contrast to those of the alkylated ones, are stable substances. Symmetrical diphenyl-*p*-phenylenediimine was described under the name of azophenylene by v. Bandrowski[14] as a red dyestuff. The quinhydrone-like intermediary form has been described by Piccard.[12] It is a fortu-

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(13) Clark, Cohen and Gibbs, Public Health Reports, Suppl No 54 (1926)

(14) Von Bandrowski, *Monatsh.*, 8, 475 (1887)

nate circumstance that in this case the substances produced at each stage of oxidation are both stable compounds. The difficulty in obtaining good titration curves consists only in the insufficient solubility of the diamine itself in aqueous media. Yet the solubility in acetic acid is satisfactory. It is not necessary to work in water-free acetic acid. A mixture of 90% glacial acetic acid and 10% water is sufficient and offers the advantage of a higher electric conductivity. Diphenyl-*p*-phenylenediamine was dissolved in the medium and titrated with a solution of bromine in the same medium. The potentials showed scarcely any drift except toward the end of a titration, and an easily reproducible curve could be obtained.

TABLE V

DIPHENYL-*p*-PHENYLENEDIAMINE–HCl

Solvent, 90% acetic acid. Oxidant, bromine, in the same solvent. *P*H, –0.49 (90% HAc).[a] Concn. = 1 mg./20 cc.

1st step: $E = 0.592 + 0.0601 \log \frac{\% \text{ oxid.}}{100 - \% \text{ oxid.}}$

2nd step: $E = 0.795 + 0.601 \log \frac{\% \text{ oxid.}}{100 - \% \text{ oxid.}}$

1st step % oxid.	Observed potential	Calcd. potential	2nd step % oxid.	Observed potential	Calcd. potential
10 2	+0.5405	+0.5386	12.2	+0.7375	+0.7436
31.1	.5735	5727	37.6	.7820	.7819
40.0	.5830	.5825	62.6	.8080	.8083
54.5	.5980	.5977	81.4	.8230♀	.8330
70.0	.6155	.6147	98.0	.8355♀	.8660
86 5	.6395	.6404			

♀ signifies drift of the potential

[a] The PH has been calculated from the potential of the hydrogen electrode as though it were an aqueous solution.

These experiments show both steps of the oxidation, and these two steps do not overlap as in the case of Wurster's dyes, but are separated by a distinct jump (Fig. 3 and Table V). So, the normal potentials of both steps of the oxidation can be determined and they were found also to be independent of the initial concentration of the substance. The slope of the curve for each step was precisely the one expected for a one-electron system.

3. The **Benzidine** Compounds.—Much time was devoted, without success, to a search for some benzidine compound which might give a non-drifting potential curve at any PH in which the green intermediary oxidation form is developed in any solvent. We tried benzidine, o-tolidine, tetramethylbenzidine, dibromotolidine and tetrabromobenzidine. It may be mentioned that in very acid solution with tolidine a regular titration curve could be obtained as in any ordinary dyestuff without any intermediary green form. This is a confirmation of the statement made by Clark, Cohen and Gibbs.[13]

4. **γ,γ'-Dipyridyl** and Dimethyl-dipyridylium Chloride.—When γ,γ'-dipyridyl, dissolved in diluted acetic acid, is reduced by chromous chloride, a deep violet color is developed. The substance so produced has been

studied by Dimroth and Heene[15] and found to be on the oxidation level of a quinhydrone, intermediary between dipyridyl and a hypothetical dihydrodipyridyl. It is easily reoxidized to dipyridyl. When the reduction is performed with a still stronger reductant, zinc dust, the reduction goes through this violet stage to a second colorless stage, and this second reduction is irreversible. It is obvious from these remarks that the potential range even of the first step of reduction lies in a hydrogen overvoltage range. Thus it is not surprising that we could not obtain trustworthy potential curves by reducing γ,γ'-dipyridyl with chromous chloride.

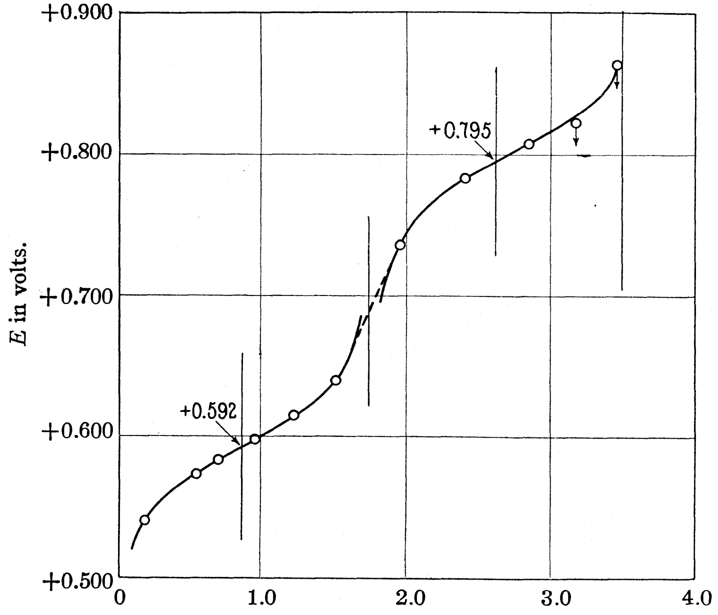

Fig. 3.—Titration curve for diphenyl-p-phenylenediamine in 90% acetic acid: ordinates, potentials referred to the normal hydrogen electrode; abscissas, cc. of bromine solution.

The violet dye can be produced only in moderately acid solutions. According to the reasoning presented in the general part of this paper, the radical should be stable only in the form of a univalent cation. It thus appeared probable that an increase in the basic character of the radical would increase its stability. Since the quaternary ammonium bases derived from pyridine are more strongly basic than the original substance, we examined an alkylated dipyridyl. When N,N'-dimethyl-γ,γ'-dipyridylium chloride was reduced a deep blue color was developed, with one distinct absorption band, the maximum of absorption being 602 mμ,

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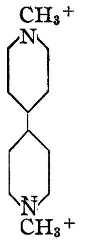
(15) Dimroth and Heene, *Ber.*, **54,** 2984 (1921); Dimroth and Frister, *ibid.*, 66, 3693 (1922).

whereas that of the unsubstituted γ,γ'-dipyridyl dye is 582 mμ. According to expectation this dye was developed also in alkaline solution, and in this case sodium hydrosulfite could be used as a reductant. The reductive titration of this quaternary ammonium compound in alkaline solution with sodium hydrosulfite gave very distinct potential curves. The potentials were instantaneously established and showed only a slow drift even in strongly alkaline solutions. Titration experiments, when performed not too slowly, gave reproducible titration curves which leave no doubt about the interpretation. The colorless solution turns blue on adding the reductant and the end of the first step of titration is recognizable by a jump of the potential to a more negative level. The second titration curve cannot be completed because it lies in the range of hydrogen overvoltage even in alkaline solution.

The slope of the titration curve for the first step of reduction is the one for a one-electron system. If it is true that the original substance has the molecular size of a dipyridyl compound, then the blue, reduced form must have the same molecular size and hereby it is proved that this blue dye is also a semiquinone-like radical. The normal potential was —0.446 volt according to the best experiments performed by rapid titration and this result varied, between PH 8.4 and 13, no more than might be expected in systems of a not entirely stable nature, namely, only by a few millivolts. This observation suggests that the normal potential is independent of PH and, according to the PH, therefore, is in the hydrogen overvoltage range in acid solution, but is in the well measurable potential range in alkaline solution. The assumption of the independence of PH can be theoretically justified by the following argument. This compound, being a quaternary ammonium base, will be ionized even in alkaline solution and may be formulated both in acid and in alkaline solution as in Formula I, which represents a bivalent cation. The reduction consists in the acceptance of one electron, which will be shared by the two ammonium groups as in Formula II. This is a univalent cation. It is also of the character of a very strong base and will remain ionized even in alkaline solution. As I and II differ only by an electron and not by a hydrogen atom, the normal potential will be independent of *P*H. This behavior enables us to use this ammonium compound as an oxidation-reduction indicator for a potential range in the very neighborhood of the hydrogen potential.



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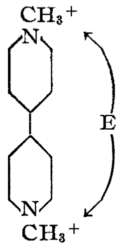

II

The above interpretation of the structure of the violet or blue dyes originating from the reduction of y,γ'-dipyridyl and related compounds is at variance with that of Emmert,[16] who considers that the compounds of the

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(16) Emmert, Ber., 53, 370 (1920)

type of dipyridyl dissociate into two radical-like molecules, just as hexaphenylethane splits into two molecules of triphenylmethyl. Our interpretation also deals with radicals but without splitting of the dipyridyl nucleus into two halves. Dimroth assumes for the violet dye, generated by reduction of γ,γ'-dipyridyl, a bimolecular formula such as was customary for Wurster's dyes. The potentiometric titration curves are at variance with this interpretation, not only for Wurster's dyes but also for that particular dipyridyl dye which was accessible to a potentiometric study. Weitz[3] was the first to advocate the radical formula.

5. Phenazine and its Derivatives.—It was a phenazine derivative which, due to its very obvious two step oxidation and its great stability in all of its three stages of oxidation–reduction, gave the impetus for this whole investigation, namely, pyocyanine, the blue dyestuff of Bacillus *pyocyaneus*.[1a] It was recognized by Wrede and Strack[17] as a phenazine derivative and was considered by these authors as a polymerization product of two molecules of a-oxy-N-methylphenazine. It was however shown by Friedheim and Michaelis[1a] that it is simply a-oxy-N-methylphenazine itself. It was shown by Michaelis[1b] that a-oxyphenazine which also was first synthetized by Wrede and Strack[17] showed the same behavior. The particular suitability of these dyes other than their stability in all forms of oxidation–reduction, consists in the fact that they are sufficiently soluble in water and accessible for titration curves in all PH ranges. This matter has been exhaustively examined in previous publications.[1a,b,c,d]

On further investigation it became manifest that many other phenazine compounds behave in the same way, with the difference that most of them are not water soluble enough, especially in the completely reduced state, to allow the use of the potentiometric method in aqueous solution, and many of those soluble in water did not show this phenomenon but behaved like ordinary dyestuffs. No phenazine dye containing an amino group showed two steps of reduction in any solvent or at any PH. The following showed no intermediary form of reduction: symmetrical and asymmetrical diaminophenazine, triaminophenazine, m-methylrosinduline, N-dimethylisorosinduline, asymmetrical anilinoaminophenazine, aminoacridine, asymmetrical aminohydroxyphenazine, rosinduline,[18] isorosinduline, phenylacridine. In contrast herewith phenazine itself and those phenazonium compounds containing no amino groups showed two steps of reduction: phenazine, a-oxyphenazine, a-methoxyphenazine, phenylnaphthazonium nitrate, phenylisonaphthazonium nitrate, methylnaphthazonium chloride, rosinduline GG (Rosindon-monosulfonate). The semiquinoid forms are green in all phenazine derivatives, and red to violet in the naphthaphenazine compounds. Many of the semiquinoid forms have been known for a

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(17) Wrede and Strack, Z. *physiol. Chem.*, 181, 58 (1929); *Ber.*. 62, 20.51 (1929)

(18) Not to be confused with Rosinduline GG of the paper quoted (1b).

long time and have been described by Claus[19] for phenazine, by Kehrmann[20] for methylphenazonium compounds, for which, after a discussion between Kehrmann and Hantzsch,[21] the meriquinoid character of the intermediary form was accepted.

The best specimen for a potentiometric study is phenazine itself. In 80% acetic acid, the reduction by hydrogen in the presence of colloidal palladium does not lead to a complete reduction because the potential of the dye system overlaps with the potential of hydrogen of one atmosphere pressure. Phenazine, dissolved in 80% acetic acid, practically colorless, first turns intensely green on reduction with hydrogen, then the green becomes paler but never disappears completely. An oxidative titration curve, therefore, shows only the end of the first step of oxidation and then jumps into the potential range of the second step, which is obtained in its full extent. When dissolved, however, in 50% acetic acid plus 50% water, the dye is reduced by palladium plus hydrogen, through the green intermediary stage to the colorless stage. This reduced solution, on oxidative titration with quinone, shows in its full extent the potential curve for both steps, as shown in the experiment (Table VI). These potentials are perfectly stable. The slope for each step of the titration is precisely the one calculated for a one-electron system.

TABLE VI

PHENAZINE

PH, 1.26 (50% acetic acid). Oxidant, quinone in 50% acetic acid

1st step

$$E = -0.086 + 0.0601 \log \frac{\%\ \text{oxid.}}{100 - \%\ \text{oxid.}}$$

2nd step

$$E = 0.254 + 0.0601 \log \frac{\%\ \text{oxid.}}{100 - \%\ \text{oxid.}}$$

1st step			2nd step		
% oxid.	Observed potential	Calcd. potential	% oxid.	Observed potential	Calcd. potential
3.1	−0.0000	−0.0036	6.8	+0.1905	+0.1860
7.5	+ .0225	+ .0206	20.0	.2190	.2179
15.3	+ .0420	+ .0415	31.5	.2345	.2340
24.0	.0565	.0560	42.6	.2465	.2463
33.5	.0680	.0682	58.8	.2630	2632
44.0	.0800	.0798	75.1	.2810	.2827
55.3	.0910	.0915	84.06	.2955	.2970
67.1	.1040	.1045	97.7	.3340	.3410
80.2	.1210	.1224			
92.8	.1465	.1514			

Summary

The analysis of the potentiometric oxidation or reduction curves for various classes of semiquinoid dyestuffs shows that always the semiquinoid form differs from the holoquinoid by one electron without any change of

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(19) Claus, *Ann. Chem.*, 168, 13 (1873); *cf.* also Hinsherg and Garfunkel, *ibid* . 292, 260 (1896); Eckert and Steiner, *Monatsh.*, 35, 1153.

(20) Kehrmann and Danecki, *Ber.*, 47,270 (1914); Kehrmann, *ibid.*, 46,344 (1013); *ibid.*, 46, 3003 (1913).

(21) (a) Hantzch, *Bn.*, 49, 511 (1916) (in which the radical structure *of* the quinhydrones is advocated for the first time); (b) *ibid..* 46, 682 and 1925 (1913)

the molecular size. Semiquinoids are radicals in which one electron is shared by two atoms which possess each a septet of electrons, alternately supplemented to an octet by the odd electron. Several cases are made accessible to a potentiometric study by the application of an organic solvent, acetic acid. Stable and titrable semiquinoids could be demonstrated in the following classes of organic substances: the alkylated diamines, the phenylated diamines, phenazine and many of its derivatives except those containing an amino group, and γ,γ'-dipyridyl and the quaternary ammonium base derived from it.

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The Ternary System: Palmitic, Margaric and Stearic Acids

BY R. L. SHRINER, J. M. FULTON AND D. BURKS, JR.

The occurrence of palmitic and stearic acids as constituents of many oils, fats and waxes is well established. Margaric acid, the intermediate C_{17} acid, has been reported in numerous natural products[1] but many investigators have denied that this odd carbon acid exists in nature.[2]

The difficulty in establishing the presence of margaric acid in mixtures of fatty acids arises from the fact that the freezing point curves for palmitic and stearic acids indicate compound formation.[3] This compound of approximately equimolecular amounts of palmitic and stearic acids melts at nearly the same temperature as margaric acid. Moreover, the equimolecular mixture of palmitic and stearic acids is stated not to be separable by fractional crystallization.[4] Even the status of margaric acid prepared by some synthetic methods has been questioned. This is of importance because of the proposed use of the synthetic glyceryl trimargarate (Intarvin) as a food for diabetics.

The purpose of the present investigation was to make a complete study of the ternary system composed of mixtures of palmitic, margaric and stearic acids. Such a study would not only indicate the possible compounds formed between these acids but also show the effect of the addition of margaric acid to the compound of palmitic and stearic acids. Com-

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(1) A review to 1912 is given by Bomer and Limprich, *Z Untersuch. Nahr. Genus.*, 23, 641 (1912); Hébert, *Bull. soc. chim.*, [IV] 11, 612 (1912); [IV] 13, 1039 (1913); Klimont, Meisl and Mayer, *Monatsh.*, 35, 1115 (1914); 36, 281 (1915); Jacobson and Holmes, THIS JOURNAL, 38, 485 (1916); Lipp and Kovács, *J. prakt. Chem.*, 99, 243 (1919); Lipp and Casimer, *ibid.*, 99, 256 (1919); Dunbar and Brunneweis, THIS JOURNAL, 42, 658 (1920); Trillet, *Ann. Physik*, 6, 1 (1925); Sekito, *Z. physiol. Chem.* 199, 225 (1931).

(2) Heintz, *Pogg. Ann*, 84, 238 (1851); 87, 21 (1852); 87, 553 (1852); 102, 257 (1857); Heiduschka and Felser, *Z. Untersuch. Nahr. Genus.*, 38, 241 (1919); Heiduschka and Luft, *Arch. Pharm.*, 257, 33 (1919); Holde, *Ber.*, 34, 2402 (1901); 35, 4306 (1902); 38, 1247 (1905).

(3) De Visser, *Rec. trav. chim.*, 17, 182 (1898).

(4) De Visser, *ibid.*, 17, 346 (1898); Heintz, *Pogg. Ann.*, 102, 257 (1857)

pound formation has been reported for mixtures of n-eicosanoic and stearic,[5] lignoceric and stearic, and lignoceric and palmitic acids,[6] but in all these cases pairs of acids containing an even number of carbon atoms have been involved. No information is available on the behavior of mixtures of higher fatty acids with odd and even numbers of carbon atoms other than occasional mixed melting points.

Experimental

Palmitic Acid.—One hundred grams of crude bayberry wax was placed in a three-liter round-bottomed flask. To this was added two liters of ethyl alcohol and 30 g. of sodium hydroxide dissolved in 50 cc. of water. The mixture was refluxed vigorously for two hours. Alcohol was distilled until foaming interfered. The contents of the flask were then placed in a porcelain evaporating dish and evaporated to dryness on a steam-bath.

The sodium salt was powdered and washed with two 800-cc. portions of ether. The salt was then dissolved in six liters of hot water and the solution filtered. The hot solution was acidified with sulfuric acid. On cooling the acid solidified and was removed. The crude cake was melted and washed with 500 cc. of 2% warm sodium bicarbonate solution. The solid cake obtained on cooling was recrystallized from 400 cc. of acetone with the aid of norite. The first crop of material weighed 70 g. and melted at 55". This material was then recrystallized from acetone six times, after which no further change in melting point or neutral equivalent took place. Colorless crystals were obtained, m. p. (capillary tube) 62.2–62.4°. A determination of the neutral equivalent gave the value 256.0; calcd. for $C_{16}H_{32}O_2$: 256.2.

Margaric Acid.—This acid has been prepared by the oxidation of diheptadecyl ketone produced by the distillation of barium stearate.[7] This method obviously yields a mixture of margaric and stearic acids. Le Sueur[S] oxidized heptadecyl aldehyde obtained from a-hydroxystearic acid. Margaric acid may also be obtained from the latter by direct oxidation or by heating silver stearate with iodine and fusion of the heptadecyl alcohol with alkali.[10]

An attempt was made to prepare margaric acid by treating cetylmagnesium bromide with carbon dioxide.[11] The product obtained by this procedure melted at 59–60" and consisted of beautiful lustrous plates. Examination showed, however, that this material was not pure margaric acid at all but contained over 41% dicetyl, $C_{32}H_{66}$, and considerable cetyl alcohol. Treatment of this mixture with alkalies and extraction of the solution with ether or benzene failed to remove all the impurities because of the soapy nature of the solutions. Margaric acid having the correct neutral equivalent and melting point could not be obtained from this mixture.

In order to obtain margaric acid of unquestionable purity it was synthesized by the following series of reactions: cetyl alcohol → cetyl bromide → cetyl cyanide → margaric acid. This method has been used before[12] and yields margaric acid which cannot be contaminated with palmitic or stearic acids since each of the intermediates may be carefully purified.

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(5) Morgan and Bowen, J. *Soc. Chem. Ind.*, 43, 346 (1924).

(6) Meyer, Brod and Soyka, *Monatsh.*, 34, 1127 (1913); Meyer and Beer, *ibid.*, 34, 1202 (1913).

(7) (a) Krafft, *Ber.*, 12, 1668 (1879); 15, 1687 (1882); (b) Meyer and Beer, *Monatsh.*, 33, 311 (1912).

(8) Le Sueur, J. *Chem. Sot.*, 85, 827 (1904); 87, 1888 (1905).

(9) Levene and West, J. Bid. *Chem.*, *16*, 475 (1913).

(10) Heiduschka and Ripper, *Ber.*, 66, 1736 (1923).

(11) Ruttan, *Intern. Congr. App. Chem. Appendix*, 25, 431 (1912).

(12) Heintz, Ref. 2; Kohler, *Jahresb.*, 9, 579 (1856); Becker, *Ann.*, 102, 209 (1857); v. Braun and Sobecki, *Ber.*, 44, 1464 (1911); Holde, Ref. 2; Levene and Taylor, *J. Biol. Chem.*, 59, 905 (1924).

Preparation of Cetyl Bromide.—One hundred and ninety grams of cetyl alcohol was placed in a 3-liter, round-bottomed flask. To this was added 350 g. of hydrobromic–sulfuric acid mixture made by passing sulfur dioxide through a mixture of 165 g. of bromine and 190 g. of cracked ice. Fifty-five grams of concentrated sulfuric acid was added to the above mixture. The mixture was then refluxed as vigorously as possible for twelve to fifteen hours.

The reaction mixture was cooled and the layers separated. The top layer was dissolved in ether and washed with water five times. The ether solution of cetyl bromide was dried with calcium chloride and the ether distilled. The oil remaining was distilled in *vacuo* and the fraction which boiled from 150–190° (2–3 mm.) was collected.

Refractionation gave pure cetyl bromide boiling at 165–170° (2–3 mm.), yield 160 g., 54% of the theoretical.

Preparation of Cetyl Cyanide.—A mixture of 152 g. of cetyl bromide, 40 g. of potassium cyanide and 5 g. of potassium iodide in 1500 cc. of 95% ethyl alcohol was refluxed for fifty-five hours. The solution was diluted with 500 cc. of water and cooled. The cetyl cyanide was separated and washed with 250 cc. of cold 50% sulfuric acid, then with water and 2% sodium bicarbonate solution. Vacuum distillation gave 100 g. of material boiling from 170–180 at 2 mm. (80% of the theoretical). The crude distillate was dissolved in warm acetone and the solution cooled in ice. Pure colorless crystals of cetyl cyanide separated;[13] m. p. 29.5–30°; d_{35}^{35} 0.8306; n_D^{35} 1.4451; yield 40% of the theoretical.

Hydrolysis of Cetyl Cyanide to Margaric Acid.—The cetyl cyanide (50 g.) was hydrolyzed by refluxing with 25 g. of sodium hydroxide in 95% alcohol for ten hours. About one-half the alcohol used for hydrolysis was distilled and the solution was cooled in an ice-salt bath. The sodium salt was filtered and washed with cold acetone and alcohol. The salt was suspended in hot water and acidified with 15% hydrochloric acid. The mixture was cooled and the acid separated as a solid cake. It was filtered and washed with a large volume of warm water.

The acid, when cooled, melted at 56–57.5°. Recrystallization from ligroin gave colorless crystals, m. p. 59.9–60° (capillary tube); yield 39 g. Determination of the neutral equivalent gave 272.6; calcd. for $C_{17}H_{34}O_2$, 270.2.

Stearic Acid.—Eastman stearic acid was found to be quite pure. It was recrystallized three times from acetone; m. p. 69.6–69.8" (capillary tube). The neutral equivalent was 285.0; calcd. for $C_{18}H_{36}O_2$, 284.3. Further recrystallization did not change these values.

Determination of Freezing Points.—The freezing points of the mixtures were determined in the apparatus similar to that used for determination of molecular weights by the freezing point method. In order to secure supercooling of the samples it was found necessary to maintain the outside constant temperature bath 3° below the freezing point of the particular sample used. The degree of supercooling of the sample permitted was 0.2–0.3°. If a greater degree of undercooling took place the sample was melted and the determination repeated. A Bureau of Standards thermometer calibrated to 0.1" was used which permitted estimations of the temperature to 0.05°. In each determination a plot of time vs. temperature was made and from this curve the true freezing point was obtained corrected for the degree of undercooling by extrapolation. All mixtures were made up determinately by weighing the amounts of each component The data obtained are summarized in Tables I–IV and represent true freezing points in which the solid and liquid phases are in equilibrium. Each freezing point given is the result of several readings, and the maximum error in reproduction of the freezing points was 0.05". It should be noted that the freezing points in Tables I–IV represent definite temperatures and are quite different from the usual capillary melting

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(13) Phillips and Mumford, *J. Chem. Soc.*, 1732 (1931).

point ranges given in the above experimental part and which are ordinarily quoted as criteria of purity.

FREEZING POINTS OF BINARY MIXTURES

TABLE I

(Data plotted in Curve I)

Palmitic, mole	Stearic, mole	Freezing point, °C.
0.0	1.0	68.40
.1	0.9	66.25
.2	.8	63.65
.3	.7	61.20
.4	.6	58.15
.5	.5	55.90
.6	.4	55.40
.7	.3	54.00
.8	.2	54.85
.9	.1	57.50
1.0	.0	60.70
.47	.53	56.10
.75	.25	53.95
.725	.275	53.60

TABLE II

(Data plotted in Curve II)

Palmitic, mole	Margaric, mole	Freezing point, °C.
0.0	1.0	59.35
1	0.9	58.10
.2	.8	56.95
.3	.7	56.35
.4	.6	55.85
.5	.5	55.50
.6	.4	55.30
.7	.3	55.95
.8	.2	57.15
.9	.1	58.80
1.0	.0	60.70

TABLE III

(Data plotted in Curve III)

Margaric, mole	Stearic, mole	Freezing point, °C.
0.0	1.0	68.40
.1	0.9	66.90
.2	.8	65.30
.3	.7	83.75
.4	.6	82.30
.5	.5	61.40
.6	.4	60.65
.7	.3	59.95
.8	.2	59.35
.9	.1	59.30
1.0	.0	59.35

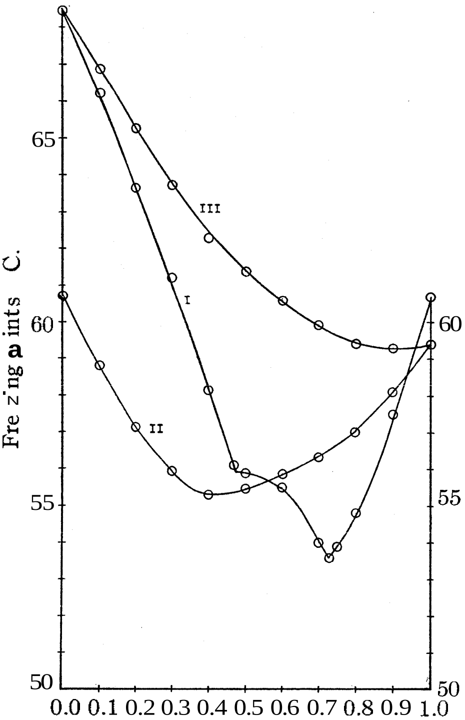
TABLE IV

FREEZING POINTS OF TERNARY MIXTURES

Palmitic, mole	Margaric, mole	Stearic, mole	Freezing point, °C.
0.8	0.1	0.1	56.00
.6	.2	.2	53.65
.4	.3	.3	55.40
.2	.4	.4	58.00
.2	.2	.6	60.10
.3	.3	.4	56.60
.4	.4	.2	55.05
.2	.6	.2	56.95
.3	.4	.3	66.25
.4	.2	.4	55.70
.6	.1	.3	54.40
.7	.1	.2	53.50
.6	.3	.1	54.20
.4	.1	.5	56.00
.7	.2	.1	54.50

Discussion

Curve I, which shows the freezing points of mixtures of palmitic and stearic acids, possesses a transition point which clearly indicates the formation of a compound. Since the compound decomposes at or near its melting point it is difficult to state its exact composition but it appears to be very close to an equimolecular mixture of the two acids. The eutectic temperature for palmitic and stearic acids is 53.6°, at a composition of 0.725 mole of palmitic and 0.275 mole of stearic acid. This value was first obtained graphically and then checked experimentally. The time–temperature curves were carefully studied to see if a second halt or transition temperature could be observed but none could be found with certainty.



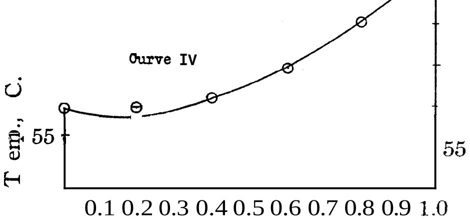
Moles palmitic, curve I. Moles margaric, curves II, III.

1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0
Moles stearic, curves I, III. Moles palmitic, curve II.

Fig. 1.

Curves II and III show no indication of compound formation between the C_{16} and C_{17} acids or C_{17} and C_{18} acids, respectively. No definite eutectics are formed and Curves II and III belong to the case in which continuous mixed crystals are formed in the solid phase.[14] This fact indicates that the separation of margaric acid from palmitic acid and especially from stearic acid would be very difficult.

The ternary mixtures were plotted according to the method of Roozeboom[15] and the three-dimensional space model constructed. This space model showed several interesting features. In the first place the ternary eutectic point was shifted very close to the palmitic acid axis and occurred at 0.68 mole palmitic, 0.16 mole margaric and 0.16 mole stearic acids, the freezing point being 52.9°. In the second place the convexity of the surface due to the compound between palmitic and stearic acids disappeared rapidly as margaric acid was added to this mixture.



Margaric, moles.

0.5 0.45 0.4 0.35 Palmitic 0.2 0.15 0.1 0.05 0.0
+
0.5 0.45 0.4 0.35 Stearic 0.2 0.15 0.1 0.05 0.0

Fig. 2.

Curve IV shows the freezing points of margaric acid with the equimolecular mixture of stearic and palmitic acids. It will be

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(14) Findlay, "The Phase Rule," Longmans, Green and Co., New York, 1923, p. 148.

(15) Roozeboom, *Z. physik. Chem.*, **15**, 147 (1894).

noted that the drop in freezing point along this curve is not very great, the minimum occurring at 0.15 mole margaric, 0.425 mole stearic and palmitic acids and freezing at 55.75°. While this drop would be readily detected by accurate freezing point determinations, it would pass unnoticed in the ordinary mixed melting point determination.[7b] A mixture of 0.15 mole of margaric acid with 0.425 mole of stearic and 0.425 mole of palmitic was made up and its melting point determined by the ordinary capillary tube method. The observed melting point range was 57.6–60.6°. The relationship between the melting points[16] of the pure acids, compounds and mixtures is shown in Table V.

TABLE V

CAPILLARY MELTING POINTS

		M. p., °C.	
		Softens at	Liquid at
1	Pure palmitic acid	62.2	62.4
2	Pure margaric acid	59.9	60.0
3	Pure stearic acid	69.6	69.8
4	Equimolecular mixture of palmitic and stearic acids	57.5	60.0
6	Remelt temperature of (4) (compound)	58.0	59.0
6	Compound (5) plus margaric acid	56.6	59.6
7	Palmitic (0.425), stearic (0.425), margaric (0.15)	57.6	60.6

The melting points given in the literature for margaric acid[1,2] vary from 54 to 60°. Hence it is easily seen how the equimolecular mixture of palmitic and stearic acids may be mistaken for margaric acid and why mixed melting points are not conclusive evidence for identification. The data in Table V also show how greatly these temperatures obtained by the ordinary capillary tube method differ from the true equilibrium temperatures recorded in Tables I–IV.

Summary

The freezing points for the ternary system of palmitic, margaric and stearic acids have been determined.

URBANA, ILLINOIS

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[16] The melting points were determined in an open beaker fitted with a mechanical stirrer. The temperature was raised at the rate of 0.5° per minute.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

The Preparation of Tri-Para-Tolylselenonium Chloride by Means of the Friedel-Crafts Reaction with Selenium Dioxide[1]

BY JOHN HARLAND CROWELL WITH W. E. BRADT

Introduction

In 1927 Lyons and Bradt[2] reported the results of a study upon the action of selenium dioxide and benzene in the presence of anhydrous aluminum chloride. Di-*p*-chlorophenyl selenide, diphenyl selenide, diphenyl diselenide and diphenylselenonium dichloride were obtained. They represented these substances as secondary products, and assumed the first product of the reaction to have been diphenyl selenoxide.

In the present work the authors carried out this reaction with toluene. The conditions of Lyons and Bradt were so modified that excess heating was avoided throughout both the reaction and the isolation procedure. This gave tri-p-tolylselenonium chloride as the chief product of the reaction.

Experimental Part

One hundred and sixty cc. of purified toluene was added to 60 *g.* of commercial anhydrous aluminum chloride which had been thoroughly mixed with 50 *g.* of freshly prepared pure selenium dioxide in a flask equipped with a reflux condenser and a means of vigorous agitation. The reaction was first cooled and then was heated for two hours on a steam-bath. The product was then hydrolyzed by pouring it into a large volume of cold water acidified with hydrochloric acid, filtered and the toluene layer removed.

The toluene layer[3] on distillation yielded small amounts of *p*-chlorotoluene (identified by a mixed melting point at 5.5–6.5° (corr.) with purified *p*-chlorotoluene).

Zinc Chloride Addition Compound.—The addition of zinc chloride solution to the warm aqueous layer caused the formation of a voluminous white crystalline precipitate which, after crystallization from alcohol, exhibited a constant melting point of 235°. It was identified as a *zinc* chloride *addition compound of tri-p-tolylselenonium chloride.* Molecular weight data, while not conclusive (due to partial ionization), indicated that two molecules of the selenium compound were attached to one molecule of zinc chloride, as in the formula, $ZnCl_2 \cdot 2(p\text{-}CH_3C_6H_4\text{-})_3SeCl$.

Anal. Calcd. for $C_{42}H_{42}Se_2Cl_2 \cdot ZnCl_2$: mol. wt., 912; C, 55.26; H, 4.64; Se, 17.37; Zn, 7.17. Found: mol. wt., 690; C, 54.3; H, 4.69; Se, 17.45; Zn, 7.15.

The zinc chloride addition compound was slightly soluble in ethyl alcohol, distilled water and aqueous hydrochloric acid. Its very slight solubility in aqueous hydrochloric acid made possible a fairly accurate determination of the amount of tri-*p*-tolylselenonium chloride formed. By this means 77% yields were isolated.

Tri-p-tolylselenonium chloride was isolated from the aqueous layer of a duplicate experiment by repeated extraction with chloroform, evaporation to a small volume and precipitation by pouring into a large volume of anhydrous ether. This, after crystalliza-

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(1) Presented at the Regional Meeting of the Pacific Division of the American Association for the Advancement of Science at Pullman, Washington, June, 1932.

(2) Lyons and Bradt, Ber., 60, 60–63 (1927).

(3) If temperature conditions were maintained at sufficiently low levels (40–70°) the toluene layer contained either only a trace of or no selenium compounds.

tion from pyridine and subsequent crystallization from acetone or chloroform, yielded clear white rhombic needles melting at 160.0° (corr.). Analysis indicated that the substance was tri-p-tolylselenonium chloride carrying one mole of water of crystallization.

Anal. Calcd. for ($C_{21}H_{21}SeCl \cdot H_2O$): mol. wt., 405.8; C, 62.09; H, 5.71; Se, 19.52; Cl, 8.73. Found: mol. wt., 404.0; C, 62.24; H, 5.79; Se, 20.43; Cl, 8.72.

These data agree with the formula reported by Leicester and Bergstrom.[4] Tri-*p*-tolylselenonium chloride was soluble in water, dilute aqueous hydrochloric acid, pyridine, chloroform, aqueous sodium hydroxide and acetone, and was very slightly soluble in ether. It formed addition compounds with chlorides of the following ions: Hg^{++}, Cu^{++}, Ag^{+}, Zn^{++}, Pb^{++}, of which only the zinc chloride compound was investigated.

Further proof of the identity of this compound was furnished by the identification of its thermal decomposition products. When tri-p-tolylselenonium chloride was heated to a temperature of 200–235° decomposition resulted. The decomposition products were purified and identified as *di-p-tolyl* selenide and p-chlorotoluene.

Anal. Calcd. for ($C_{14}H_{14}Se$): C, 64.3; H, 5.40; m. p., 69–69.5°. Found: C, 63.5; H, 5.39; m. p. 68.0° (corr.).

Di-p-tolylselenide was moderately soluble in alcohol, chloroform, ether, carbon disulfide and insoluble in water.

The zinc chloride addition compound of triphenylselenonium chloride, $ZnCl_2 + 2(C_6H_5)_3SeCl$ (m. p. 273.5–274.0°), was prepared by using the authors' modified method with benzene. Analyses for C, H, Se, Zn and Cl completed its identification. Only traces of the products reported by Lyons and Bradt were found. This compound will be further discussed in a later paper.

Discussion

A comparison of the benzene compounds obtained by Lyons and Bradt with the toluene compounds by the authors using a procedure modified to avoid excess heating, verifies the original assumption by Lyons and Bradt that diphenyl selenide, diphenyl diselenide and di-*p*-chlorophenyl selenide were secondary products, the formation of which had been caused by the action of the heat upon the original products. The introduction of vigorous mechanical agitation, careful limitation of temperature to 40–70°, and the use of excess toluene, has avoided this thermal decomposition of the original products. Consequently, tri-p-tolylselenonium chloride, or triphenylselenonium chloride normally constitutes the entire reaction product. In no case were appreciable amounts of the products analogous to those identified by Lyons and Bradt found to be present. The presence of di-*p*-tolyl selenide and p-chlorotoluene in small amounts has been explained by the fact that they are known to be products of the thermal decomposition of tri-p-tolylselenonium chloride.

Summary

A method has been described for the synthesis of tri-p-tolylselenonium chloride by the action of selenium dioxide on toluene in the presence of anhydrous aluminum chloride. The presence of small amounts of di-*p*-tolyl selenide and *p*-tolyl chloride is due to the thermal decomposition of the

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(4) *Leicester* and Bergstrom, THIS JOURNAL, **53**, 4428-4436 (1931).

tri-*p*-tolylselenonium chloride which has been isolated in 77% yield as the zinc chloride addition compound.

PULLMAN, WASHINGTON
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Wildiers' Bios: The Fractionation of Bios from Yeast[1]

BY W. LASH MILLER, EDNA V. EASTCOTT AND J. E. MACONACHIE

The fractionation of the bios contained in an aqueous infusion of malt-combings was described by Dr. G. H. W. Lucas[1a] in 1924. After preliminary purification of the infusion, baryta and alcohol were added and the precipitate so formed was filtered off; to the filtrate, freed from alcohol and barium, he gave the name "crude Bios II solution." The precipitate was extracted with hot water, and the solution freed from barium; this "crude Bios I solution" was then precipitated by lead acetate and ammonia, the precipitate suspended in water and treated with carbon dioxide and sulfuric acid; the solution so obtained, after removing the last traces of lead with hydrogen sulfide, he called "Bios I solution." The physiologically active constituent of this Bios I solution was identified with *i*-inositol by Miss E. V. Eastcott[2] in 1925.

The yeast crop resulting under standardized conditions when a solution of salts and sugar is seeded with certain kinds of yeast[3] is not much increased by adding either Bios I solution (*i. e.*, a solution of i-inositol) or Bios II solution; but if both are added together, the crop is large—Lucas[1a] obtained counts of 15 to 25 from his Bios I solutions, 35 to 50 from his Bios II solutions purified by acetone, and 165 to 240 from the mixtures. In Wildiers' language, neither Bios I (*i*-inositol) nor Bios II contains much bios, but their mixture contains a considerable quantity of that substance; thus precipitation by alcohol and baryta "fractionated" the bios of the combings, and has subsequently been used to fractionate the bios from malt, rice polishings, tea, mushrooms (*agaricus campestris*), molasses, tomatoes, oranges and yeast. It is obvious that such a fractionation of the bios is very different from the mere removal of inactive materials,

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[1] Financial assistance from the National Research Council of Canada is gratefully acknowledged.

[1a] G. H. W. Lucas, J. Phys. Chem., 28, 1180 (1924).

[2] E. V. Eastcott, ibid., **32,** 1094 (1928); THIS JOURNAL, **51,** 2773 (1929).

[3] Dr. Helen Stantial finds that Wildiers' yeast and the following yeasts from the American Type Culture Collection behave with inositol and Bios II like the race with which most of our own experiments have been carried out: 2361 Sacch, ***validus***, 4206 ***Schizosacch, octosporus.*** Mr. Maconachie found the same for 2331 (brewers' yeast) and for 2335 (bakers' yeast) and Dr. Lucas (Ref. 1a, p. 1190) for one of the yeasts used by Prof. W. H. Eddy. Miss Stantial also found that 2361 Sacch. ***pastorianus*** gives a large crop in media containing only salts and sugar [see Lash Miller, J. Chem. Ed., **7,** 263 (1930)] like the top yeast used by Prof. Eddy (Lucas, Ref. 1a); and that the crops of 2333 Sacch, ***mandschuricus*** and of 2602 ***Zygosacch, mandschuricus*** are much increased by Bios II, but are not further increased by adding inositol to media containing Bios II. (Helen Stantial, Trans. Roy. Soc. Canada. Sec. III, p. 163 (1932).

(e. g., by precipitation with alcohol, etc.); it would prevent confusion if the word "purification" were used when processes of the latter type are meant.

Experiments with Bios II solutions prepared from malt combings, from tomatoes, and from yeast, show that these solutions also can be fractionated;* the provisional names "Bios IIA" and "Bios IIB" are proposed for their constituents—the former for that which is left behind, and the latter for that which is adsorbed when, after preliminary purification if necessary, the Bios II solution is shaken with charcoal. Thus, up to the present, three separable constituents of Wildiers' bios have been recognized, via., Bios I (i.e., inactive inositol), Bios IIA and Bios IIB. Media containing salts, sugar, and only one of these constituents give a small yeast crop; in media containing any two of them the crop is also fairly low; but if the medium contains all three constituents the crop is large, as shown in Table XI, which gives the crops obtained with Wildiers' yeast. This method of fractionating Bios II was described at the May meeting of the Royal Society of Canada; the present paper gives some details of the work with yeast.

I. Apparatus and Procedure

The technique followed in these experiments is substantially that described in detail in Miss Eastcott's paper,[2] except that dextrose[5] was used instead of cane sugar in the culture media, and that the seed yeast was cultivated in a tomato medium[6] instead of in wort.

Culture media, seeded to a count of 1 or 2 with a race of yeast whose isolation is there described, were rocked for twenty-four hours in a thermostat at 25° after which a measured volume was pipetted into a centrifuge tube containing chloroacetic acid, and the crop determined from the height of the yeast column after centrifuging. By the "count" is meant the number of cells in 4 X 10^{-6} cc.; 250,000 times the count gives the number of cells in one cc. of the culture medium. Except where otherwise stated, the inositol used was Eastman's ash-free inositol, and the Bios II was from a stock prepared on the large scale from malt combings.

Rocker-tubes

These are L-shaped glass tubes, closed at one end, which are rocked (in the plane of the L) thirty times a minute through an angle of 60° in the water of a thermostat. A size convenient for 10 cc. of culture medium is 27 cm. long and 14 mm. inside diameter; tubes of about the same length, but 27 mm. in diameter, are used for 50 cc. of solution.

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(4) Miller, Eastcott and Sparling, *Trans. Roy. Soc. Canada*, Sec. III, p. 165 (1932).

(5) It is only when the medium contains nothing but sugar and salts that the trace of bios contained in a good brand of cane sugar seriously affects the crop. Eastman's "practical dextrose" gives the same low crops as the more expensive "dextrose" if it has been cleaned by shaking 100 g. with 100 cc. of a mixture of 10 volumes of acetone with one volume of water. A second washing is hardly necessary; not much dextrose is dissolved.

(6) 4 g. KH_2PO_4, 2 g. $MgSO_4 \cdot 7H_2O$, 8 g. NH_4NO_3, 0.7 g. $CaCl_2 \cdot 6H_2O$, 2 g. Rochelle salts, 100 g. cane sugar, water to one liter, to this is added 300 cc. of tomato juice, obtained by heating the contents of a can of tomatoes to 100°, filtering through cloth and paper, and neutralizing half of it to litmus with about 5 cc. of 2 *N* sodium hydroxide. This is easier to make than wort, and yeast cultivated in it is white, not dark colored.

If the culture medium, seeded with yeast, be left in a stationary flask instead of being rocked in a rocker-tube, the cells form a layer at the bottom of the flask; as this layer grows thicker, the upper cells more and more shut off the supply of sugar, salts, oxygen and bios from those below, and hinder the escape of alcohol and acid formed by them. Even the topmost cells are supplied only by diffusion and by accidental convection currents; and because of the small concentration of bios in media used for crop determinations, the diffusion of that component is particularly slow. That under such conditions the twenty-four-hour count may depend more on the shape and size of the vessel and the volume of the culture medium than on the quantity it is intended to measure (*viz.*, the amount of bios present), is shown by the results of Table I.

In these experiments the rocker-tube and the flasks were immersed in the water of the same thermostat; with one exception each contained 50 cc. of a medium made of 25 cc. of S. & S. (p. 1504, note 7) 23 cc. of water and 2 cc. of wort, seeded with Yeast 2331 of the Am. Type Cult. Coll'n whose rate of reproduction is practically the same as that of the yeast commonly used here; the smallest flask was supplied with only 40 cc. of the same medium; if it had been filled to the neck the count would doubtless have been lower still.

Stopping the rocker lowers the count, but doubling the usual rate of rocking leaves the count unchanged; 10 cc. in the small rocker-tube gives the same count as 50 cc. of the same medium in the larger tube. Thus there is ample evidence that results obtained in rocker-tubes are independent of diffusion, while those obtained in flasks may be much influenced by that factor.

Table I

Rocker-tube	C = 270	125-cc. Erlenmeyer	C = 93
260-cc. Erlenmeyer	169	50-cc. Erlenmeyer	60
200-cc. Erlenmeyer	112		

With our yeast the twenty-four-hour count in the 250-cc. Erlenmeyer agrees with that in the rocker-tube if the latter does not exceed 100; when the count in the rocker-tube is larger, that in the flask may catch up if it be left standing long enough, as shown in Table II.

In the experiments of Table II, the 50 cc. of medium in each vessel contained 5 cc. of wort; only one rocker-tube was used, but seven flasks, as it would obviously have been impossible to take samples from a single flask without shaking it.

Table II

Hours after seeding	14.3	16.2	17.2	19.8	24.6	38.4	48.5
Rocker-tube	C = 170	232	288	345	430	444	446
250-cc. Erlenmeyer	C = 138	165	193	242	300	427	445

Sugar and Salts.—Clark's sugar and salts solution[7] was used; when bios is present, moderate changes in the proportions and absolute amounts

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(7) 15 *g.* KH_2PO_4, 7.5 *g.* $MgSO_4 \cdot 7H_2O$, 30 *g.* NH_4NO_3, 2 5 g. $CaCl_2$ $6H_2O$, and 360 g. dextrose, in 1800 cc.; 5 cc of this "S & S." (2.5 cc. in the half-strength medium of Tables III and IV) was used in each rocker-tube, and made up to 10 cc by the other ingredients of the culture medium

of the salts do not matter very much; although, as Fulmer[8] has shown, in absence of bios they may be of the first importance. Cutting down Clark's quantities of salts and sugar to half does not affect counts below 250–300; but Miss Reader's[9] *streptothrix* medium (with one per cent. of dextrose) is too dilute for yeast counts as high as 100.

The results of Table III were obtained with different quantities of the same bios (p. 1509) in the half-strength Clark's medium and in Miss Reader's medium; those of Table IV with a constant amount of bios in half-strength Clark's medium and in media containing up to five times the salts and sugar of Miss Reader's.

TABLE III

Proportionate amount of bios	1	2	3	4
Clark's medium, half strength	C = 125	175	225	283
Miss Reader's medium	C = 83	110	123	125

TABLE IV

Miss Reader's medium, *C* =	125	Miss Reader's medium × 4, C =	221
Miss Reader's medium × 2	170	Miss Reader's medium X 5	271
Miss Reader's medium × 3	200	Clark's half strength	283

Acidity of the Culture Medium.—The P_H of Clark's medium (equal volumes of S. & S. and water) is 4.6, about the same as that of wort; while addition of 4 cc. of water and one cc. of $N/8$ sodium hydroxide to 5 cc. of S. & S. gives a nearly neutral medium, $P_H = 6.8$. In the experiments described below, counts were determined both with and without the addition of this much alkali to the medium before seeding; those to which alkali has been added are the "neutral media," the others "Clark's media."

It is clear from the results of Tables VI to XII that there is no "best" initial P_H for media containing bios; high twenty-four-hour counts are often higher in the initially neutral medium, low counts often lower. This behavior is no doubt due to the formation of acid in the medium while the crop is growing; carbon dioxide does not lower the P_H of Clark's medium, but even so low a count as 27 may be accompanied by *a* change of P_H from 4.6 to 3.6 or from 6.8 to 5.8, and higher counts increase the acidity much more. Addition of sodium bicarbonate or replacement of part of the acid phosphate by dibasic phosphate has, of course, the same effect as addition of sodium hydroxide; high counts can also be improved by adding certain salts, which probably act as buffers.

For example, a count of 200 in Clark's medium with wort as source of bios was raised to 325 by adding sodium hydroxide in the proportion given above, ammonium mucate raised it to 329, sodium lactate to 330, sodium potassium tartrate to 360, sodium acetate to 291, sodium chloride had no effect; the amount of salt used in each case con-

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(8) **Fulmer,** Nelson and Sherwood, THIS JOURNAL, 43, 191 (1921).

(9) 0.10 g. KH_2PO_4, 0.016 g. K_2HPO_4 (to bring Pa to 7.4), 0.07 g. $MgSO_4\ 7H_2O$, 0.30 g. $(NH_4)_2SO_4$, 0.05 g $NaCl$, 0.04 g. $Ca(NO_3)_2$ and 0.5 g. dextrose, in 100 cc. This medium was worked out by Miss V. Reader [*Biochem. J.*, **21,** 904 (1927)] for *streptothrix corallinus*, not for yeast; she found that the dextrose might be varied from 0.6 to 2.0%; one per cent. was used in the experiments of Tables III and IV above.

tained metal or ammonium equivalent to that in the hydroxide; the medium to which sodium hydroxide had been added was not further improved by adding acetate, lactate or tartrate.

This whole matter is being further investigated.

II. Crops from Yeast Infusions, with and without Inositol

Workers in other laboratories have confirmed Miss Eastcott's observation that adding inositol does not much improve the yeast crop obtained from sugar and salts solutions; and Williams[10] with his co-workers, and Narayanan,[11] report little or no improvement when inositol is added to media containing sugar, salts and yeast-infusion or certain other yeast preparations. These preparations (made from Fleischmann's starch-free yeast, and from brewers' yeast, respectively) thus resembled the juice of oranges or grapes, the infusions of bran, dried catnip, cottonseed meal or saffron, and the solutions of meat extract (lemco) or dried milk (klim), studied by Miss Eastcott; for she found[2] that any one of the latter added to salts and sugar solution gave a good yeast crop which was not appreciably improved by adding "Bios I" as well. In view of these results we were quite unprepared for Mr. Maconachie's observation that an aqueous infusion[12] made from a pure culture of Yeast No. 2335 of the Am. Type Cult. Coll'n gave in Clark's medium a twenty-four-hour count of 125, but on addition of 0.02 mg./cc. of Eastman's ash-free inositol a count of 234; the yeast whose crop was measured was the same as that from which the infusion had been made, *viz.*, No. 2335.

Mr. Maconachie then prepared an extract[13] from brewers' yeast (for which we are indebted to the O'Keefe Brewing Company of Toronto), following the procedure of Narayanan.

One cc. of this extract in 10 cc. of culture medium seeded with a brewers' yeast (Am. Type Cult. Collection No, 2331) gave a twenty-four hour count of 440, which was increased to 500 by adding 0.02 mg./cc. of Eastman's inositol.

On centrifuging in a Sharples laboratory centrifuge, 680 g. of this same yeast yielded 350 cc. of beer (*i. e.*, culture liquid); thus rather less than half of this sample of "brewers' yeast" consisted of yeast cells, and a considerable part of the "yeast extract" made from it was really beer extract.

One cc. of the beer in 10 cc. of culture medium gave a count of 248, which was not increased by adding inositol but was raised to 474 by adding an amount of Bios II from

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(10) Williams, Warner and Roehm, THIS JOURNAL, **51**, 2764 (1929).

(11) Narayanan, Biochem. J., **24**, 6 (1930).

(12) 2.5 liters of sugar and salts solution (p. 1504, note 7) mixed with 2 liters of water and 500 cc. of a strong wort (Eastcott, Ref. 2, p. 1097), seeded with 50 cc. of a suspension of Yeast 2335 (count 150), and stirred for twenty-four hours at room temperature, gave a crop of count 450. The yeast was filtered out, heated with 150 cc. of water to 100° for three hours, and filtered. The cloudy filtrate was autoclaved for a few minutes and the resultant precipitate removed by centrifuging.

(13) 3.7 kg. of the yeast as received was heated to 65° for four hours with 2.9 liters of 93% alcohol, and the residue after filtration was similarly extracted first with 3 liters and then with 2 liters of 50% alcohol. The combined filtrates were evaporated in *vacuo* to 1350 cc.

combings which by itself (in the 10 cc.) gave a count of 50; this shows that the beer contained a large excess of inositol. On the other hand, one cc. of an extract made (as described above) from the thoroughly washed yeast cells gave a count of 488, which was raised to 660 by adding 0.02 mg./cc. of inositol, but was *left* unchanged by Bios II.

Thus the extract made from the cells was deficient in inositol, but in the original "yeast extract" this deficiency was largely made up by the excess of inositol introduced with the beer.

These observations suggested an explanation for Narayanan's negative results, *viz.*, that his brewers' yeast may have contained a little more beer than ours, or beer a little richer in inositol. If this were the case, adding inositol to his extract would not have improved his yeast crops; for as Miss Eastcott has shown, addition of inositol beyond a certain amount (which depends on the quantity of Bios II in the medium) does not go on increasing the crop.

That this is not the only possible explanation, however, was shown by the behavior of the next batch of yeast obtained from the same brewery. This yielded only 16% of beer, as compared with over 50% from the first batch; and neither the beer, nor the extract from the yeast as received, nor the extract from the washed yeast-cells was improved as a culture medium by adding inositol. Neither was the extract prepared from a pure culture of the race of yeast used in most of the experimental work of this laboratory; but whereas for Maconachie's preparation Yeast 2335 was freshly cultured, that of our own race was taken from the bottom of a culture-flask two days after seeding, when (as shown by crop determinations) most of the Bios II had been removed from the wort. That the amount and quality of the bios in a yeast extract depends upon the condition of the cells used to make it, is evident from the results with Fleischmann's yeast described below; it follows even more directly from an observation of Maconachie, who found that the extract prepared from cells of No. 2335 which had been stirred for twenty-four hours with salts and sugar gave a count of only *35* instead of 125.

Two half-pound cakes of Fleischmann's yeast were then purchased, one (I) from the Canada Bread Co., and the other (II) from Fleischmann's agency in Toronto; neither gave the iodine test for starch. An aqueous extract and a 50% alcoholic extract was prepared from each; and the twenty-four-hour counts given in Table V were obtained in Clark's medium containing the extract from 0.05 g. of yeast cake per cc., either with or without 0.02 mg. of Eastman's inositol per cc.

TABLE V

0.05 g. Cake	I	Alcoholic extr., alone	C = 250	With inositol C = 275
.05 g. Cake	II	Alcoholic extr., alone	C = 155	With inositol C = **175**
.05 g. Cake	I	Aqueous extr., alone	C = 217	With inositol C = 367
.05 g. Cake	II	Aqueous extr., alone	C = 167	With inositol C = 209
.01 g. Cake	III	Extract alone	C = 100	With inositol C = 320

The Fleischmann Company then presented us with a fresh one-pound cake of starch-free yeast, Cake III, sent from their factory in Montreal in a refrigerator car.

This was chopped up into 2 liters of boiling water, left in a steam-box for two hours with occasional shaking, autoclaved for an hour, and filtered. The filtrate was evaporated *in vacuo* to 175 cc., 350 cc. of alcohol added, the precipitate filtered off, and the solution (mixed with 50 cc. of washings) evaporated to dryness in a vacuum. The residue, dissolved in water, neutralized with a few drops of normal sodium hydroxide, and made up to 180 cc., is the extract whose fractionation is described below; one cc. corresponds to 2.5 g. of yeast cake.

The extract made from this cake contained much more bios per gram of yeast, and a much larger excess of Bios II, than the preparations from either of the other yeast cakes; the counts given in Table V were obtained with only one-fifth the weight of yeast used in the other cases.

Table VI gives the counts obtained when each cc. of the culture medium contained the extract from 0.01 g. of yeast cake III together with from $^1/_{800}$ to $^1/_{25}$ milligram of the Eastman Company's "ash-free inositol."

TABLE VI

Extract from 0.01 g. of yeast per cc. of medium

Inositol	Mg./cc. =	0.00125	0.0025	0.0050	0.010	0.020	0.040
Clark's medium	C =	170	200	260	294	320	316
Neutral medium	C =	163	217	300	370	410	410

Miss Eastcott has already shown that there is such a thing as "enough" inositol for a given amount of Bios II, *i. e.*, more does not increase the yeast crop. The experiments of Table VI show that 0.02 mg./cc. together with that in the extract used, is enough inositol for the Bios II contained in that extract; the reason why inositol did not improve the crops given by the extracts of Williams and of Narayanan is simply that these extracts themselves contained enough inositol for their Bios II.

As the suggestion has been made (though not supported experimentally) that the results obtained by Miss Eastcott with Kahlbaum inositol and with her own preparations from tea might be due to some unspecified impurity (which if it exists must have been present in equal quantity in all of them), we have subjected both Kahlbaum (pre-war) inositol and Eastman ash-free inositol to the process used in purifying Miss Eastcott's inositol from tea; that is, each of them was heated for twenty hours to 110° with 22% hydrochloric acid, and after evaporating to remove the acid, was fractionally crystallized and recrystallized from mixtures of methyl alcohol and water. The counts obtained with these purified inositols, both alone and with Bios II from various sources, agreed within the experimental error with those given by the commercial preparations.

Table VII gives the counts obtained with Kahlbaum inositol, Eastman ash-free inositol (both as purchased) and Miss Eastcott's original preparation from tea, when 0.02 mg./cc. of each in turn was added to media containing per cc. the extract from ten milligrams of yeast cake III (*i.* e., $Y/\text{cc.} = 0.01$).[14] The counts agree with each other and with the two corresponding determinations of Table VI (Eastman inositol) as closely as can be measured with the technique employed.

TABLE VII

Yeast extract $Y/\text{cc.} = 0.01$, with inositol 0.02 mg./cc.

Clark's med.: Eastman's, $C = 324$; Kahlbaum's, $C = 320$; from tea, $C = \mathbf{326}$
Neutral med.: Eastman's, $C = 416$; Kahlbaum's, $C = 400$; from tea, $C = 410$

III. Fractionation of the Bios from Brewers' Yeast by Baryta and Alcohol and by Lead Acetate and Ammonia

Both extracts from the first batch of brewers' yeast (*viz.*, that from the yeast as it was received, and that after the beer had been removed) on treatment with baryta and alcohol as described by Lucas, yielded "crude Bios I" and "crude Bios II" solutions just like those from the other eight sources of bios enumerated above. It seemed worth while, however, to repeat these experiments with the extract from the second batch, which like Narayanan's extract gave as large a crop without inositol as with it. Following Narayanan's procedure, the extract was autoclaved with baryta solution and the filtrate after removing the barium was precipitated with acetate of lead. Like the extract itself, neither the baryta-filtrate nor the lead-acetate-filtrate[15] (after removing metals and acetic acid, neutralizing, adding water salts and sugar as usual, and seeding with yeast) gave a larger yeast crop when inositol was added than without it. But when, after autoclaving the extract with baryta, *two volumes of alcohol were added before filtration,* the result was very different: 0.02 mg. of Eastman inositol added to each cc. of the culture medium in which this filtrate was used, raised the count from 140 to 340. The reagent generally used for precipitating inositol[16] is basic lead acetate with ammonia; and when the filtrate from the neutral lead acetate precipitation was precipitated with this reagent, the count obtained from this basic-lead-acetate-filtrate was raised from 110 to 325 by adding 0.02 mg./cc. of inositol.

Neither of these reagents for precipitating inositol was used by Narayanan in preparing his "concentrates;" and so, naturally enough, he "obtained no evidence to support Eastcott's claim that inositol is an essential constituent of bios."

IV. Details of the Fractionation of Bios from Fleischmann's Yeast by Baryta and Alcohol, and by Charcoal

Because of its large content of Bios II, the extract from Cake III was chosen for these experiments; the preparation of the extract is described on p. 1508.

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[14] The symbol $Y/\text{cc.}$ means the number of grams of yeast cake used to make the preparation contained in one cc. of culture medium.

[15] Used in the experiments of Tables III and IV.

[16] Needham, Biochem. *J.*, 17, 422 and 431 (1923).

Table VIII gives the counts obtained with the extract from 0.0025–0.040 g. of yeast per cc. of culture medium; the counts from media containing the extract from 0.01 g. of yeast per cc. together with various amounts of inositol have been recorded in Table VI.

TABLE VIII

	Y/cc. = 0.0025	0.005	0.010	0.020	0.040
Clark's med.	C = 62	70	108	160	260
Neutral med.	C = 114	124	120	142	274

The Baryta-Filtrate

In each of several *50-cc.* Erlenmeyer flasks, 2 g. of powdered crystallized barium hydroxide and 10 cc. of extract (from 25 g. of yeast) were heated to 100° for three hours with occasional shaking. After cooling, the contents of one flask were filtered and the precipitate washed with **5** cc. of hot water; filtrate and washings were heated and 6.25 cc. of *2* N sulfuric **acid** added (just enough to change the color of Congo paper), the barium sulfate was removed by filtration and volatile acids by repeated evaporation in *vacuo*, the residue was neutralized by sodium hydroxide, and made up to 25 cc. Thus one cc. of this "baryta-filtrate" comes from one gram of yeast.

For equal values of Y/cc., the counts obtained with baryta-filtrate are much lower than those with extract; this can hardly be due to the presence of a poison in the former, because when added to a medium containing wort it increased the count (wort alone, C = 350; wort with bar.-filt. Y/cc. = 0.0375, C = 434). Adding Bios II does not increase the Count (Y/cc. = 0.0125, neut. med., C = 142; with Bios II, 138), adding inositol, however, does (see Table IX); thus in the baryta-filtrate as in the extract there is excess of Bios II, but some of the latter has been destroyed by the baryta treatment. Table IX gives the counts obtained in neutral media containing 0.02 mg./cc. of inositol and various amounts of the baryta-filtrate.

TABLE IX

Bar.-filt.	Y/cc. = 0.0025	0.005	0.010	0.0125
Neutral med.	C = **36**	54	130	225

There is much more difference between the forty-eight-hour counts and the twenty-four-hour counts when the media contain baryta-filtrate than when they contain yeast extract; moreover, after suitable treatment with acid the baryta-filtrate gives higher twenty-four-hour counts. These experiments, which suggest that the Bios II of the extract is not irrecoverably destroyed by the baryta treatment, are being extended; they may throw light on changes which some of the solutions undergo when kept.

Fractionation by Precipitation with Baryta and Alcohol

To the contents of another of the 50-cc. Erlenmeyer flasks (see *baryta-filtrate,* above) as soon as it was taken from the steam-bath, 20 cc. of 95% alcohol was added, with shaking; after standing for some hours the contents were filtered, and the precipitate washed with 15 cc. of a mixture of two volumes of alcohol and one of water, filtrate precipitate and washings being kept separate. **A** "crude Bios II" solution was prepared from the filtrate, by removing barium and volatile acids (as described above) and neutralizing;

the washings were treated in the same manner; and a "crude Bios I" solution was prepared from the precipitate by extracting with **15** cc. of hot water and treating this filtrate like the other; each of the three was brought to a volume of **25** cc., *viz.*, one cc. per gram of yeast used in making them. A mixture of equal volumes of these three solutions gave practically the same count as the baryta-filtrate from the same amount of yeast (neutral medium, Y/cc. = **0.0125,** bar.-filt., C = **142,** mixture, C = **136);** with **0.02** mg./cc. inositol, the mixture gave a somewhat lower count (bar.-filt., C = **225,** mix., C = 178), suggesting loss of Bios II.

Counts from the "crude Bios I solution" were not increased by adding inositol, but were increased by adding Bios II from combings, and the opposite is true for counts from the "crude Bios II solution" (see Table X, 0.02 mg./cc. inositol was used). Thus bios from Fleischmann's yeast is fractionated by baryta and alcohol just like bios from brewers' yeast and from the other eight sources enumerated on p. 1502.

TABLE X

Crude Bios I,	Y/cc. = **0.02**	Clark's med.:	C = **20**	With Bios II	C = **143**
Crude Bios I,	Y/cc. = **0.02**	Neutral med.:	**C** = **24**	With Bios II	C = **158**
Crude Bios II,	Y/cc. = **0.02**	Clark's med.:	C = **60**	With Inositol	**C** = **264**
Crude Bios II,	Y/cc. = **0.02**	Neutral med.:	**C** = **120**	With Inositol	C = **263**

Fractionation of the yeast extract itself, omitting the baryta treatment, gives a better yield of Bios II.

The crude Bios **II** solution obtained by adding 2 g. of baryta (dissolved in **3** cc. of hot water) and **26** cc. of alcohol to **10** cc. of yeast extract (from **25** g. of yeast), gave a count of **340** instead of the **263** of Table **X** (Y/cc. = **0.02,** inositol **0.02 mg./cc.,** neutral medium).

The preparation of crude Bios II solution can be still further simplified, by extracting the yeast (6 lb. Fleischmann's starch-free) with 80% alcohol (6 liters) and adding baryta (360 g. dissolved in 360 cc. of water) and alcohol (750 cc. 95%) to the filtrate, which of course contains water taken from the yeast cake.

The counts from a crude Bios **II** solution prepared in this way by Mr. A. J. Mueller were: Y/cc. = **0.014,** C = **350;** Y/cc. = **0.028,** C = **444** (both with **0.02** mg./cc. of inositol in Clark's medium). This preparation therefore was better than that from the baryta-filtrate, though not so good as that obtained by directly fractionating the extract from Cake III.

Fractionation of the Bios II by Charcoal

One gram of Darco charcoal was shaken for fifteen minutes with **30** cc. of a solution containing one cc. of 2 N sulfuric acid and the crude Bios **II** solution (that of Table X) from **20** g. of yeast, filtered off, and washed with **15** cc. of water; the filtrate was shaken with another half gram of charcoal, which was filtered off and washed as before. The combined filtrates and washings were freed from sulfuric acid by baryta, and made up to **80** cc.; each cc. of this neutral "crude Bios IIA solution"[17] came from **0.25** g. of the

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(17) **This is the correct designation according to the nomenclature of Lucas' paper; but in the present paper (except where otherwise stated), this was the solution used in the experiments for which quantities of Bios IIA or IIA are given. Similarly Bios IIB or IIB are printed when the crude Bios IIB solution was used.**

yeast cake. The charcoal from the two operations was shaken for half an hour with 40 cc. of freshly prepared "acetone–ammonia reagent,"[18] filtered off, washed with 10 cc. of the reagent, and then shaken again with 25 cc. of the reagent and washed as before. The united extracts and washings were evaporated in *vacuo* and the residue dissolved in water to a volume of 25 cc.; this "crude Bios IIB solution" was neutral to litmus, each cc. came from 0.80 g. of yeast.

With 0.02 mg./cc. or 0.04 mg./cc. of inositol, whether in Clark's medium or in the neutral medium, and whether Y/cc. = 0.01, 0.04 or 0.05, the crude Bios IIA solution gave counts of 20 or lower, and the crude IIB solution gave counts of 50 to 60 or lower. But when IIA (Y/cc. = 0.01) and IIB (Y/cc. = 0.01) and inositol (0.02 mg./cc.) were present in the same (neutral) medium, the count was 127. *Thus charcoal fractionates Bios II into Bios IIA and Bios IIB, just as baryta and alcohol fractionates bios into Bios I and Bios II.* Mr. Mueller's crude Bios II solution (p. 1511) was fractionated in the same way; the counts (with 0.04 mg./cc. of inositol in neutral media) obtained from his IIA and IIB separately and together, are given in Table XVI.

To make quite sure that it was "Wildiers' bios" that had been fractionated, and not some other "nutrilite,"[19] the media of Table XI were seeded with Wildiers' own yeast, a culture of which was courteously furnished us by Professor R. J. Williams of the University of Oregon.

The inositol used in these experiments (0.04 mg./cc.) was Eastman's; the Bios IIA (Y/cc. = 0.04) and the Bios IIB (Y/cc. = 0.02) were the crude solutions whose preparation from the baryta-filtrate has just been described in detail.

TABLE XI

(Wildiers' yeast)	Clark's medium	Neutral medium
Inositol	C = 20	C = 30
Bios IIA	13	20
Bios IIA + inositol	25	50
Bios IIB	42	38
Bios IIB + inositol	92	62
Bios IIA + Bios IIB	30	98
Bios IIA + Bios IIB + inositol	262	225

A series of measurements was carried out in which increasing amounts of Bios IIB were added to media containing excess of inositol and a fixed amount of Bios IIA, and another in which the amount of Bios IIB was kept constant and that of Bios IIA was varied; the results are given in Table XII. In Clark's medium (but not in the neutral medium) the counts first rise and then fall again as the amount of Bios IIB is increased; it is proposed to determine the nature and the amount of the acid to whose formation this behavior is probably due.

When a considerable amount of the variable constituent has been added, the effect of further additions is small (Table XII); just as when inositol is

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[18] Acetone–ammonia reagent: 5 cc. of conc. ammonia, 35 cc. of water, acetone to 200 cc.

[19] Williams and Bradway, THIS JOURNAL, 53, 783 (1931).

TABLE XII

Inositol 0.04 mg./cc.

Bios IIA. Y/cc =	0.0025	0.005	0.01	0.02	0.04	0.08	
Bios IIB Y/cc. = **0.01,** C =	54	74	178	230	270	....	**Clark's**
Bios IIB Y/cc. = **0.01,** C =	54	60	127	179	220	....	**Neutral**
Bios IIB Y/cc. = **0.02,** C =	......	65	140	280	306	**340**	**Clark's**
Bios IIB Y/cc. = **0.02,** C =	......	54	118	278	360	**418**	**Neutral**
Bios IIB, Y/cc. =	0.0025	0.005	0.01	0.02	0.04	**0.08**	
Bios IIA Y/cc. = 0.01, C =	100	156	178	140	150	....	**Clark's**
Bios IIA Y/cc. = **0.01,** C =	92	116	127	118	187	....	**Neutral**
Bios IIA Y/cc. = **0.02,** C =	......	150	230	280	228	217	**Clark's**
Bios IIA Y/cc. = **0.02,** C =	......	113	179	278	396	390	Neutral

added to the yeast extract (Table VI) or to Bios II solutions (Table V of Miss Eastcott's paper)[2] or when Bios II is added to a solution of inositol. On this behavior we hope to base a method for determining Bios IIA and Bios IIB in arbitrary units, which will enable their amounts in Bios II solutions from different sources to be compared, even before these constituents have been obtained in the pure state—although, of course, attempts to isolate and identify them are being made.

The interesting discovery of Professor O. R. Richards,[20] that one part of thallium per million of Williams' culture medium[21] increases the count of Yeast 2335, led to the experiments with Kahlbaum thallium–potassium alum whose results are given in Table XIII. For, although the twenty-four-hour counts obtained by Richards with thallium were small, so are those with inositol under similar circumstances; and just as inositol exerts its full effect only in the presence of Bios II, so might the counts with thallium be heightened by addition of inositol and one of the constituents of Bios II. The results, however, show that this is not the case, and that neither Bios IIA nor Bios IIB owes its potency to thallium.

TABLE XIII

Thallium 0.001 mg./cc., **Inositol** 0.04 mg./cc.

Bios IIA, Y/cc. = 0.02: Clark's **medium** C = 15, **Neutral medium** C = **15**

Bios IIB, Y/cc. = 0.02: Clark's **medium** C = 40, **Neutral medium** C = **40**

V. Identity of Constituents from Different Sources

Miss Eastcott's work with bios from sixty different sources, the fractionation by baryta and alcohol of bios from nine sources, and the fractionation by charcoal of Bios II from three sources,[4] make it probable that there is only one bios and not "a whole category" of them, as Wildiers thought possible. This probability is increased by the results of Table XIV which show that mixtures of inositol (in excess) with Bios IIA from any one of the three sources and Bios IIB from either of the other two, give large counts; so, whether chemically identical or not, the constituents from the

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(20) O. R. Richards, J. *Biol. Chem.*, **96, 405** (1932).

(21) 2 g. KH_2PO_4, **0.25 g** $MgSO_4$, **3 g.** $(NH_4)_2SO_4$, **0.25 g.** $CaCl_2$, **1.5 g. asparagine (Eimer and Amend), 20 g. sucrose, one liter of water.**

three sources are at least physiologically interchangeable. Work now in progress on the behavior of these constituents with acids and bases, with organic solvents, and on acetylation,[22] will no double reveal any differences that may exist; although the isolation and identification of the active principles of these obviously impure solutions is, of course, the main object of the investigation.

TABLE XIV

Inositol 0.04 mg./cc.

	IIB (*Y*/cc. 0.02)		IIB (tomato)		IIB (combings)		No Bios IIB	
	Clark	Neut.	Clark	Neut.	Clark	Neut.	Clark	Neut.
IIA (*Y*/cc. 0.04)	304	396	284	286	286	237	20	20
IIA (tomato)	300	324	284	230	280	214	37	35
IIA (combings)	220	212	187	162	233	150	15	19
No Bios IIA	50	60	54	60	57	52	..	..

Closer examination of Table XIV shows that the counts[23] in neutral media (where relations between count and amount of constituent in the medium are simpler than they are in Clark's, see Table XIII) increase toward the left of each line and toward the top of each column; *i.e.*, the three lines agree in saying that most IIB was added with the yeast preparation and least with that from combings, and the three columns agree that the order of the amounts of IIA is the same.

With the data at present available it is not possible to make an accurate computation, but as a rough approximation the amounts of Bios IIA from tomato and from combings, respectively, used in these experiments, correspond to *Y*/cc. = 0.025 and *Y*/cc. = 0.016; and the amounts of Bios IIB to *Y*/cc. = 0.014 and *Y*/cc. = 0.010.

VI. Presence of Bios IIA in Crude Bios I Solutions

That the Crude Bios I solutions from combings and from tomatoes must contain some active constituent other than Bios I (*i.e.*, inositol) forced itself on our attention long ago; the same is true of the Crude I from yeast; for as is shown by the results of Table XV, higher counts can be obtained from media containing Bios II by adding Crude Bios I solution than by adding inositol; the preparations used are those of Table X. The experiments of Table XVI show that this substance is Bios IIA; for adding IIA to the Crude I leaves the count unchanged, while adding IIB greatly increases it.

The Crude I of these experiments is that of Tables X and XV; the IIA and IIB used as reagents were prepared from Mr. Muellers' Bios II (p. 1512 above), the quantities used per cc. of medium came from 0.03 g. of his yeast cakes.

As previous experiments had shown that Lucas' "Bios I solution" does not contain Bios IIA, it seemed probable that that substance could be found in the filtrate after precipitating "Crude Bios I solutions" with lead acetate and ammonia. Experiments with the Crude Bios I solution from tomatoes show that this is the case; the IIA and IIB of Table XVII are those of Table XVI, details of the treatment of the tomato juice are given in

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(22) E. M. Sparling, *Trans.* Roy. *Soc. Canada, 22,* Sec. III, p. 271 (1928).

(23) Those in media containing all three constituents are meant.

TABLE XV

Neutral Medium

Crude Bios I (Y/cc. = 0.10), with 0.02 mg./cc. inositol	C = 50
Crude Bios II (Y/cc = 0.02). with 0.02 mg./cc inositol	263
Crude Bios II (Y/cc. = 0.02), with 0.04 mg./cc. inositol	280
Crude Bios II with the Crude I and 0.02 mg./cc. inositol	394

TABLE XVI

Inositol 0.04 mg./cc., Neutral Medium

Bios IIA	C = 12	Crude Bios I	C = 50
Bios IIB	37	Crude I and Bios IIA	54
Bios IIA and Bios IIB	334	Crude I and Bios IIB	304

TABLE XVII

Inositol 0.02 mg./cc., Clark's medium

Tomato preparation	C = 60
Tomato preparation with Bios IIA	64
Tomato preparation with Bios IIB	470

the footnote.[24] Unfortunately the time at our disposal did not permit the repetition of these experiments with the Crude Bios I solution of Table XV; that of Table XVIII had been prepared, with another object in view, by precipitating Mr. Mueller's Crude Bios I solution (see p. 1511) with lead acetate and ammonia, but as his baryta–alcohol precipitate had been washed with 50% alcohol instead of 65%, and as the barium compound of Bios IIA is more soluble than that of inositol, most of the former had been carried into the crude Bios II solution; enough remained, however, to leave no doubt as to its presence. The IIA and IIB of Table XVIII are those of Tables XVI and XVII.

TABLE XVIII

Inositol 0.02 mg./cc., Clark's medium

Yeast preparation	C = 24
Yeast preparation with Bios IIA	32
Yeast preparation with Bios IIB	92

Summary

1. Addition of inositol to media containing aqueous or alcoholic extracts of yeast may or may not increase the twenty-four-hour yeast crop, depending on the condition of the cells from which the extracts were made.

(24) Evaporated *in vacuo* 3730 cc. of filtrate from canned tomatoes to 1910 cc., added 3820 cc. alcohol; evaporated filtrate to 350 cc.. added 400 g. of baryta dissolved in 425 cc. of water, and 1600 cc. of alcohol; filtered, washed precipitate with 150 cc. of dilute alcohol (2 volumes of alcohol, one volume of water) and extracted with 1500 cc. of water. Removed barium from this Crude Bios I liquor by carbon dioxide and sulfuric acid, neutralized with ammonia, and precipitated with 100 g. of crystallized lead acetate dissolved in 100 cc. of water, and 45 cc. of conc. ammonia (11.8 N) diluted with 17 cc. of water; filtered, did not wash precipitate. Removed lead from filtrate by sulfuric acid and hydrogen sulfide, and acetic acid by repeated evaporation *in vacuo.* Diluted a portion (corresponding to 60 cc. of tomato juice) to 10 cc., shook with 0.5 g. of Darco charcoal, neutralized the filtrate with sodium hydroxide and made up to 20 cc.; thus 1 cc. came from 3 cc. of juice, this amount was present in the 10 cc. of culture medium of each experiment of Table XVII.

Before using brewers' yeast to make a yeast extract, the liquid culture medium in which the cells are suspended ought to be removed; as this liquid may contain enough inositol to render further addition of that substance to the "yeast" extract unnecessary.

2. By treating yeast extracts (from brewers' yeast and from Fleischmann's yeast) with alcohol and baryta as Lucas treated his infusion of malt combings, we have fractionated the bios contained in them; just as the bios from combings, malt, rice polishings, tea, mushrooms, molasses, oranges and tomatoes has already been fractionated.

Neither of the two fractions so obtained, added to salts and sugar medium, gives a large yeast crop; but the two together do. The crop obtained with one of them (*viz.*, the crude Bios I solution) is not increased by adding inositol, but is much increased by adding Bios II, whether the latter be derived from yeast or from malt combings. The crop obtained with the other (*viz.*, the crude Bios II solution) is much increased by adding inositol.

A similar fractionation has been effected with lead acetate and ammonia, which like baryta and alcohol precipitates inositol.

3. By shaking the crude Bios II solution from Fleischmann's yeast with charcoal, it has been fractionated into two constituents for which the provisional names "Bios IIA" (not adsorbed) and "Bios IIB" (adsorbed) are proposed. Thus the bios from yeast has been fractionated into three constituents. With salts and sugar, each of these constituents gives a small yeast crop; mixtures of any two of them give fairly small crops; but all three together give a large crop.

Bios II from malt combings, and Bios II from tomatoes have been fractionated in the same way.

4 Crude Bios I solutions, as Lucas called them, whether prepared from malt combings from tomatoes or from yeast, contain Bios IIA; but his Bios I solutions do not, for the Bios IIA remains in solution when the Crude Bios I solution is precipitated with lead acetate and ammonia.

5. The Bios IIA from yeast is physiologically equivalent to that from combings and to that from tomatoes; i. e., either of the latter with inositol and Bios IIB from yeast gives a large crop. In the same sense, Bios IIA from combings is equivalent to Bios IIA from tomatoes; and Bios IIB from any of the three sources is equivalent to Bios IIB from either of the others.

As the crude Bios IIA solutions from the three sources were obtained by the same chemical procedure, the chemical properties of their active constituents are to that extent the same; and as their effects on the yeast crop are also the same, there is at present no reason to regard them as separate species. For the same reasons there is no basis for assuming more than one Bios IIB.

Until a source of bios has been found which with alcohol and baryta does not behave like the nine already studied, or which with charcoal does not behave like the three whose behavior is described in this paper, it is unnecessary to assume the existence of more than one bios.

6. Measurements with Wildiers' yeast in media containing one of the three constituents, or two, or all three of them, show that it behaves just like Toronto yeast; there is therefore no necessity to assume the existence of a class of "nutrilites" distinct from Wildiers' bios.

The names are given of four species of yeast from the American Type Culture Collection which with inositol and Bios II from combings behave the same as Wildiers' yeast and as the Toronto yeast; and the names of three species which behave otherwise.

7. To check the spread of misapprehensions, experiments are described which show that the twenty-four-hour crop obtained with yeast extract is just as much increased by inositol bought from Kahlbaum or from Eastman as it is by that prepared by Miss Eastcott from the Bios I soln. of tea.

8. Experiments are described which show to what a great extent yeast crops obtained in stationary vessels may depend on factors other than the amount of bios in the culture medium; and some which show that the agitation and aeration afforded by Fraser's rocker-tubes are sufficient.

9. The effect of the initial PH of the culture medium on the yeast crop is discussed. In media containing bios, there is no one initial PH that in every case gives a larger crop than any other; the nature and amount of the acid or acids formed during crop determinations is being studied.

10. Professor O. R. Richards' discovery of thallium in asparagine led to experiments which show that the effects obtained with the crude solutions of Bios IIA and Bios IIB are not due to thallium; work on the isolation and identification of the active principles of these solutions is in progress.

TORONTO, ONTARIO, CANADA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Action of Phosphorus Pentachloride with Ethers

BY FRANK C. WHITMORE AND D. P. LANGLOIS[1]

Because of the failure to convert neopentyl alcohol to a neopentyl halide without rearrangement[2] other methods were sought. The ordinary methods of preparing alkyl halides involve the use of acids or the formation of acids during the process. Since some believe that acids cause rearrangement (Meerwein) a method was sought which would involve no acid at any stage in the reaction. Such a process seemed to be presented by the action of phosphorus pentachloride with an ether. This reaction might be expected to give only alkyl halides and phosphorus oxychloride. Preliminary experiments raised doubts as to the accuracy of this conception.[3] A study of the literature revealed a surprisingly small amount of work on the action of ethers with phosphorus pentachloride. Dichlorodiethyl ether gave a small amount of ethyl chloride and 1,1,1-trichloroethane.[4] The treatment of diphenyl ether and diphenyleneoxide with phosphorus pentachloride gave no recognizable products.[5] Mixed aryl alkyl ethers gave mainly chlorination products of the aryl part of the ether without splitting the ether linkage.[6]

In the present work several ethers and acetals were treated with phosphorus pentachloride. In no case was a practical yield of organic chloride obtained. Moreover, there was always a chlorinating action with the formation of hydrogen chloride. This destroyed the hope that an alkyl chloride could be formed in the absence of acid by the use of phosphorus pentachloride and an ether.

The neopentyl acetal of formaldehyde reacted with phosphorus pentachloride to give very little alkyl chloride. This was mainly if not entirely tertiary amyl chloride, a product of rearrangement.

Experimental

Preparation of Ethers and Acetals.—The following benzyl ethers were made with the indicated yields by the method of Lowe[7] using petroleum ether (60–90°) and vigorous stirring: dibenzyl ether, b. p. 198–200° (55 mm.), 46%; n-butyl benzyl ether, b. p. 217–219° (737 mm.), 34%; n-amyl benzyl ether, b. p. 237–240° (733 mm.), 51%; *sec*-amyl benzyl ether, b. p. 223–226° (735 mm.), 29%.

Neopentyl formal, $[(CH_3)_3CCH_2)]_2CH_2$, b. p. 176–177.5° (737 mm.) was obtained in 65% yield.[8]

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(2) Whitmore and Rothrock, THIS JOURNAL, **54**, 3433 (1932).

(3) Since this was written, the study on the reaction of diethyl ether with phosphorus pentachloride by Guthmann [ibid., *64*, 2938 (1932)] has appeared. This definitely proves the complexity of the reaction.

(4) Lieben, *Ann.*, ***146***, 213,218 (1868); Abeljanz, ibid., ***164***, 203 (1872).

(5) Hoffmeister, Ber., 3, 748 (1870); *Ann.*, **159**, 200, 212 (1871).

(6) Autenrieth and Muehlinghaus, Ber., *89*, 4098 (1906).

(7) Lowe, Ann., ***241***, 374 (1887).

(8) *Cf.* Conant, Webb and Mendum, THIS JOURNAL, 61, 1246 (1929).

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.2. Found: C, 70.1 and 70.6.

Di-n-butyl formal, b. p. 177–178° (734 mm.), was made in 74% yield.

The phosphorus pentachloride was heated under reduced pressure to remove any free hydrogen chloride.

Action of Phosphorus Pentachloride with the Ethers and Acetals

Diisoamyl Ether.—Commercial diamyl ether[9] was fractionated. The 172–178° fraction was dried over sodium in the cold for two days, filtered and distilled. The boiling point of the material finally used was 174–176° (735 mm.). A mixture of 52 g. (1 mol) of phosphorus pentachloride and 39.5 g. (1 mol) of diisoamyl ether was heated on a water-bath under a reflux condenser. Much hydrogen chloride was evolved and the solid dissolved completely. After six hours the mixture was cooled. A loss in weight of 17 g. indicated the evolution of about 0.5 mole of hydrogen chloride. The mixture was decomposed with ice, separated and the oil was washed with water, with sodium carbonate solution, again with water and then dried two days over anhydrous sodium sulfate and fractionated carefully through a 27 × 0.8 cm. packed column,[10] using a reflux ratio of 20:1. A total of 27.5 g distilled from 50 to 168" without any constant fraction even after several redistillations. The entire experiment was repeated several times with the same result. No evidence of the formation of isoamyl chloride was obtained.

Diisopropyl Ether.—The 65–69° fraction from the commercial ether[11] was dried for two days over sodium, filtered and redistilled, b. p. 67–68° (735 mm.). When the ether was refluxed for six hours with phosphorus pentachloride, it was recovered unchanged.

A sealed tube containing 10 g. (1 mol) of diisopropyl ether and 20 g. (2 mols) of phosphorus pentachloride was heated at 110° for six hours. Much hydrogen chloride escaped when the tube was cooled in ice and opened. The mixture was decomposed on ice and worked up in the usual way. Two careful fractionations gave 2 g. (24% yield) of isopropyl chloride (b. p. 35–36", 43.2% Cl). The rest boiled from 36 to 130° without any constant fraction.

Dibenzyl Ether.—The reagents (0.25 mole of each) were refluxed in an apparatus fitted to absorb the evolved gas. About 0.4 mole of hydrogen chloride was evolved (titration). The organic products obtained were 24 g., b. p. 82–86" (27 mm.), 28 g., b. p. 95–96" (25 mm.), and a semi-solid residue which was insoluble in water and ether. The first liquid was benzyl chloride as shown by its conversion to *p*-nitrobenzyl chloride, m. p. 70–71°. The second liquid was a mixture of benzal chloride and benzotrichloride. Boiling sodium hydroxide solution left an oily layer which gave the phenylhydrazone of benzaldehyde, m. p. 155–156°. The alkaline solution gave benzoic acid, m. p. 120–122°, which was converted to benzanilide, m. p. 160°. The solid product from the original reaction was refluxed three hours with normal sodium hydroxide solution. Part of it dissolved. Steam distillation gave a small amount of benzyl alcohol (3,5-dinitrobenzoate, m. p. 104–106°), and benzaldehyde. The products of the action of dibenzyl ether with phosphorus pentachloride are benzyl chloride, benzal chloride, benzotrichloride and probably a phosphate of benzyl alcohol.

***n*-Butyl Benzyl** Ether.—The products obtained from 33 g. of the ether and 2 mols of phosphorus pentachloride were 3.5 g., b. p. 77.5" (733 mm.) (38.7% Cl), 2 g., b. p. 98° (733 mm.) (47.2% Cl) and traces of benzyl chloride, benzal chloride and benzotrichloride. The first liquid fraction was n-butyl chloride in 19% yield and the second was probably impure butylidene chloride.

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(9) Supplied by the Sharples Solvents Corp., of Philadelphia.

(10) Whitmore and Lux, THIS JOURNAL, 54, 3448 (1932).

(11) Supplied by the Carbide and Carbon Chemicals Corp., of N. Y.

n-**Amyl** Benzyl Ether.—The products from 32 g. of the ether and 2 mols of phosphorus pentachloride were 3.5 g., b. p. 101–105" (716 mm.) (32.0% Cl); 6.5 g., b. p. 170–180° (716 mm.), 12.5 g., b. p. 185–187° (716 mm.) (44.6% Cl). The first was n-amyl chloride in 18% yield. The others were benzyl and benzal chlorides.

Sec-**amyl** Benzyl Ether.—From 44.5 *g*. of the ether and 2 mols of phosphorus pentachloride were obtained 4 g., b. p. 93° (716 mm.) (32.8% Cl); 6.5 g., b. p. 95.5" (720 mm.) (31.7% Cl); 7.5 g., b. p. 80–90° (27 mm.), and a viscous residue of 23 g. The first two were impure 2-chloropentane in 39% yield. Hydrolysis of the other fraction gave benzaldehyde and benzoic acid.

Diphenylene Oxide.—The treatment of 84 g. of diphenylene oxide with 2 mols of phosphorus pentachloride gave an 80% yield of a monochlorodiphenylene oxide, m. p. 94–96°.

Anal. Calcd. for $C_{12}H_7OCl$: Cl, 17.0. Found: Cl, 16.4.

Di-n-butyl Acetal of Formaldehyde.—To 160 g. (1 mol) of the acetal in a flask fitted with a reflux condenser and an absorber for hydrogen chloride was added slowly 208 g. (1 mol.) of phosphorus pentachloride. The reaction was violent and hydrogen chloride was evolved. The mixture was heated until no more gas formed and was then decomposed on ice in the usual way. The product was carefully distilled through the 27 × 0.8 cm. column at 738 mm., twelve fractions being obtained. Formaldehyde was evolved during the heating. The most important fractions were No. 2, 43 g., b. p. 77–79° (37.5% Cl) identified as n-butyl chloride by formation of the 3,5-dinitrobenzoate, m. p. and mixed m. p. 63-64', yield of *n*-butyl chloride, 23%; No. 4, 3 g., b. p. 103–110" (27.4% Cl), probably chloromethyl n-butyl ether; No. 6, 3 g., b. p. 160–165° (20.5% Cl), probably monochlorodibutyl ether; and No. 8, 26 g., b. p. 175–178°, unchanged acetal.

Di-neopentyl Acetal of Formaldehyde.—From 63 g. of the acetal and 2 mols of phosphorus pentachloride were obtained six fractions at 738 mm. Only 6 g., b. p., 85–98", was obtained in the amyl chloride range. Treatment of this with sodium hydroxide gave tertiary amyl alcohol, 3,5-dinitrobenzoate, m. p. 86–88', mixture with known 3,5-dinitrobenzoates, of tertiary amyl alcohol, m. p. 86–88°, mixed m. p. 86–88"; of neopentyl alcohol, m. p. 92–93", mixed m. p. 70–73°. The other fractions contained 15 to 21% Cl but were not identified although Fraction No. 5, 9 g., b. p. 171–173" (17.0% Cl), may have been the impure monochloroacetal.

The action of the di-neopentyl acetal of formaldehyde with phosphorus pentachloride gave small amounts of amyl chlorides. No evidence of neopentyl chloride was obtained.

Summary

1. The action of phosphorus pentachloride with several types of ethers and acetals (formals) has been studied.

2. The production of RCl from R_2O or from $(RO)_2CH_2$ and phosphorus pentachloride is small or entirely absent.

STATE COLLEGE, PENNSYLVANIA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Pentose Reactions. III. Xylan

BY CHARLES D. HURD AND NEILL R. CURRIE[1]

Xylan has been isolated from many plant materials such as straw, corn cobs, corn seedlings, esparto cellulose, etc., by extraction with 5–10% sodium hydroxide solution but oat hulls have never been studied in this connection. That oat hulls will give rise to xylose by an hydrolysis with dilute sulfuric acid has been demonstrated[2] recently. In the present work, it was found that xylan could be isolated from oat hulls in 22–24% yields. Prior removal of lignin from the hulls by treatment with phenol[3] had little effect on the quality or the yield of the xylan.

Since the phenol treatment does not remove the pentosan from the hulls, and since it was found to dissolve xylan quite readily, it seems evident that xylan does not exist as such in the plant material. Some kind of hydrolysis in the plant material is evidently caused by the hydroxide solution. The fact that xylan has been found to give cryoscopic molecular weight values[4] of 146, 195, and 231 in acetamide solutions of 0.45, 0.95 and 1.1% concentrations, respectively, points to a relatively simple molecule.

Diacetylxylan has been reported[5] to give molecular weight values of 400–633, depending on the method of acylation. In the present work diacetylxylan was prepared by interaction of xylan with acetic anhydride which contained very little nitric acid. The molecular weight, determined cryoscopically in nitrobenzene, indicated that it contained much of the monosaccharide derivative, $C_5H_6O_2(OCOCH_3)_2$. It regenerated xylan on saponification. This low molecular weight value for diacetylxylan aligns it with other polysaccharides (inulin acetate, mannan acetate, etc.) which give low molecular weight values in solvents. Pringsheim[6] has given a good review of the existing data.

Xylose was obtained by hydrolyzing the xylan with dilute sulfuric acid. It is interesting to note that a considerable conversion of an emulsion of the xylan in water into a reducing sugar was brought about by ethylene. A control experiment without the ethylene showed no such conversion. This is similar to the effect noted by Rea and Mullinix[7] with starch.

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(1) *Holder of a Quaker Oats Fellowship,* 1927–1929, *administered through the Miner Laboratories. Chicago.*

(2) *Hurd and Isenhour,* THIS *JOURNAL,* 54, 323 (1932).

(3) *Kolb and Schoeller, Cellulosechemie,* 4, 37 (1923).

(4) *Reilly, Donovan and Bums, Proc. Roy. Irish Acad.,* **B39**, *505* (1930); *Chem. Abstracts,* **25**, 1499 (1931).

(5) *Hibino, J. Chem. Soc. Japan, 61,* 417 (1930); *Chcm. Abstracts,* 25,4854 (1931).

(6) Pringsheim, "*Chemistry of the Monosaccharides and of the Polysaccharides,*" McGraw-Hill *Book Co., Inc.,* New *York,* 1932, *pp.* 291, 300–302, 312, 333–339. *See also* Haworth *and Streight, Helv. Chim. Acta,* 15, 609 (1932); Haworth, *Hirst and Percival, J. Chem Soc* , 2384 (1932).

(7) *Rea* and Mullinix, THIS *JOURNAL,* 49, 2117 (1927).

Experimental Part

Preparation of **Xylan.**—Five hundred grams of oat hulls was soaked for two days in a 2% ammonia solution, filtered off, washed and then digested for two to three hours with 6 liters of a 10% solution of sodium hydroxide. During the digestion, steam was passed through the mixture continuously. The mixture was filtered through a wire gauze and then through a cloth mat. The filtrate was added to an equal volume of 95% alcohol. After a complete mixing, another 1–2 liters of alcohol was added and the whole left overnight. The gummy alkali product was collected upon a cloth filter and washed thoroughly with alcohol. The spongy precipitate was pulverized underneath glacial acetic acid. After several hours, it was filtered off and the solid triturated with fresh acetic acid. Finally, it was collected upon a filter and rinsed free of acid with 95% alcohol; yield, 110–120 g. The xylan thus produced was a white, amorphous powder. Analysis by the colorimetric method2 showed a purity of 96.8%. Several other methods or modifications were tried but this gave the most consistent results. The pentosan content of the original hulls, analyzed colorimetrically as before, was 28.6%.

This preparation was checked by Mr. M. E. McDougle, who also determined its rotation. The xylan taken for the rotation measurements was dissolved in sodium hydroxide solution and filtered through asbestos (Gooch funnel) to remove all solids not taken out by the cloth filter The aqueous solution used for polarimetric measurements contained about equal weights of xylan and sodium hydroxide.

Rotation. 3.479 g. substance in 125, 180 and 250 cc. solution, reading, respectively, 3.94, 2.75 and 2.00" to the left in a 2-dm. tube at 30": $[\alpha]^{30}_{D}$ -70.8, -71.1, $-71.8°$, average, $-71.2°$.

Extraction with Phenol.—Oat hulls, which had stood for twenty-four hours in a 2% ammonia solution, were washed thoroughly and dried. Then a 24-g. portion was heated at 100° for six hours with 300 g. of phenol which contained 10 drops of concd. hydrochloric acid.[3] After filtering off the undissolved hulls they were washed well with water, dilute acetic acid and finally with water until the washings were free from acid This residue, after drying at 95°, weighed **13.1** g. From it, with the procedure outlined above, there was obtained 4.9 g. of xylan. This yield is 20 4% of the weight of the original hulls, which is about the same as without the phenol treatment.

All except 0.04 g. of a 0.5-g. sample of xylan dissolved in 10 *g.* of phenol which contained one drop of hydrochloric acid. After removal of the phenol from the filtrate by steam distillation, and solution of the non-volatile residue in sodium hydroxide solution, the sodium derivative of xylan was precipitated by addition of alcohol in the usual manner. The xylan which was thereby obtained weighed 0.39 g.

Xylose from the **Xylan.**—Thirty grams of xylan was refluxed for an hour with 1.2 liters of 5% sulfuric acid. Then it was filtered, the filtrate neutralized with barium carbonate, filtered, acidified slightly with phosphoric acid, filtered again and the filtrate concentrated to a thick sirup. Absolute alcohol was added and the solution seeded with crystals of xylose. Ultimately, 4.5 g of crystalline xylose, m. p. 146°, separated The sirup also contained much xylose, for it readily gave the characteristic double salt[S] of cadmium bromide and cadmium xylonate by reaction with cadmium carbonate, water and bromine.

Ethylene and **Xylan.**—Two 10-g. samples of xylan were boiled with 100 cc. of water and cooled to 22°. One of these emulsions was stoppered and left as a control. The other was saturated with ethylene, the flask stoppered and allowed to stand for three weeks. The solid material was then filtered off and washed with 20 cc. of water. An aliquot portion of the filtrate was dropped slowly into hot Fehling's solution and the mixture boiled for two minutes. By weighing the red cuprous oxide which was produced.

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(8) Bertrand, *Ber.*, **35**, 1460 (1902).

it was found that there had been a 10% conversion into a reducing sugar. The control specimen showed practically no conversion.

Diacetylxylan.—Previous workers[5,9] have synthesized this compound by heating xylan with acetic anhydride alone or with pyridine or zinc chloride. In the present work, good results were obtained by heating xylan (10 g.) for six hours at 70° with acetic anhydride (200 cc.) which contained a little nitric acid (2 cc., concd.). Prior to the heating the xylan was soaked in water for a day, filtered off and washed on the filter with glacial acetic acid. At the end of the heating, the light brown colored solution was filtered and the diacetylxylan precipitated by addition of methanol. The weight of the white, amorphous product was 8.5 g.

Anal.[10] Subs. 0.5018; acetic acid ≈ 10.47 cc. of 0.4332 N KOW. Calcd. CH_3-COOH from $C_5H_6O_2(OCOCH_3)_2$, 55.5; found, 55.1.

Diacetylxylan was soluble in nitrobenzene, aniline and quinoline; very slightly soluble in benzene and glacial acetic acid; and insoluble in carbon tetrachloride and camphor. Nitrobenzene was a suitable cryoscopic solvent.

Mol. Wt.[11] Subs. 0.0605; grams of nitrobenzene, 36.12; f. p. lowering, 0.0393°. Calcd. for $C_9H_{12}O_6$, mol. wt. 216; found, 298.

Saponification of the Diacetylxylan.—Three grams of the ester and 150 cc. of 10% potassium hydroxide solution were refluxed for two hours. The diacetate slowly dissolved. Then it was cooled and treated with alcohol till no further precipitation occurred. The brown gum was filtered off, washed with alcohol and allowed to stand overnight in glacial acetic acid. One gram of xylan was thus produced which was light brown in color.

The preparation of diacetylxylan and its saponification were also checked by Mr. M. E. McDougle. The rotation of the xylan produced by saponification of the diacetate was determined as before.

Rotation. Subs. 0.775 g. in 44 and 74 cc. of sodium hydroxide solution, reading, respectively, 2.49 and 1.50" to the left in a 2-dm. tube at 30°, $[\alpha]^{30}_{D}$ −70.6, −71.6°, average, −71.1°.

Summary

Xylan was isolated from oat hulls in 22–24% yields by extraction with sodium hydroxide solution. Evidence is offered to show that the xylan which is isolated in this way is simpler in structure than the pentosans in the original plant material. An emulsion of xylan in water was changed into a reducing sugar in about ten per cent. yields by the action of ethylene. In nitrobenzene as solvent diacetylxylan was found to have a molecular weight of about 300.

EVANSTON, ILLINOIS

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(9) Heuser and Schlosser, *Ber.*, **56**, 392 (1923).

(10) By method of Perkin, *J. Chem. Soc.*, **87**, 107 (1905).

(11) Mr. R. W. McNamee also confirmed the low molecular weight of the diacetylxylan on some material independently prepared.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Basis for the Physiological Activity of -Onium Compounds. XII. Aryl Ethers of Choline[1,2,3]

BY R. R. RENSHAW AND C. Y. HOPKINS

In a previous paper, the physiological activity[4] of the phenyl ether of choline has been described. The marked stimulating action of this substance on the respiration, and its effect upon the blood pressure, suggested to Hunt that it might have an antidotal action to narcotic poisons, particularly if the molecule could be so altered as to bring about an augmentation of certain effects. We have thought it desirable, therefore, to prepare a number of substituted phenyl ethers of choline by introducing various polar and water soluble groups in the aryl nucleus. It was thought that these groups would modify the orientation of the molecule at the adsorbing membrane and thus bring about a change in the intensity or duration of the stimulating actions. We have, therefore, prepared compounds in which a nuclear hydrogen atom has been replaced by hydroxyl, ether, ester, amino and acetamino groups. Hunt[4] has found that these groups markedly diminished the stimulating nicotine action and, in certain cases (the *p*-methoxy derivative), the activity was but little more than 5% of the activity of unsubstituted phenyl ether of choline, and that the acetamino group further greatly reduced or abolished this action.

In the preparation of these choline ethers, β-bromoethyl phenyl ethers were condensed with trimethylamine. The bromo ethers were prepared by condensing ethylene bromide with the corresponding phenol in the presence of potassium hydroxide. With the unsubstituted phenols, the method of Marvel,[5] in which the phenol is condensed by using aqueous alkali, gives excellent results, but with substituted phenols the yields are lower and the use of alcoholic alkali seems to be superior. In the case of polyphenols, there seems to be no record of the production of a monobromoethyl ether, although the interaction of the polyphenols with dihalogen alkanes has been studied by several workers. Vorländer,[6] in treating hydroquinone with sodium ethylate and varying quantities of ethylene bromide, succeeded in getting only the bis-ether and, at times, a small quantity of alkali insoluble, bromine free product. On repeating the experiment with aqueous potassium hydroxide, he reported getting an "inextricable mixture of substances." With catechol, he isolated only the ethylene ether,

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[1] This problem is being carried out in cooperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him

[2] This is the second paper constructed from a thesis presented by C. Y. Hopkins, June, 1929, for the degree of Doctor of Philosophy at New York University.

[3] The authors wish to express their appreciation to Parke, Davis & Co for a Fellowship which has made this work possible.

[4] Hunt and Renshaw, *J. Pharmacol.*, **37**, 193 (1929).

[5] Marvel and Tanenbaum, THIS JOURNAL, 44, 2647 (1922).

[6] Vorlander, Ann., 280, 203 (1894).

and with resorcinol he obtained a mixture from which nothing could be isolated.

We have found it possible, with hydroquinone, to get a yield of from 14 to 16% of the mono β-bromoethyl ether by using a methyl alcohol solution of potassium hydroxide, whereas the best yield, using aqueous potassium hydroxide, was 10%. In all cases investigated with the polyhydroxyphenol, large quantities of the diether and bis compound were formed.

$$C_6H_4(OH)_2 + C_2H_4Br_2 \longrightarrow BrC_2H_4OC_5H_4OH + (BrC_2H_4O)_2C_6H_4 + (HOC_6H_4OCH_2—)_2$$

Less thorough investigation failed to yield a mono ether of resorcinol. Attempts to obtain the desired product through the monobenzoyl derivative of hydroquinone also failed because of the easy hydrolysis of the latter substance.

Experimental Part

p-Bromoethyl Aryl Ethers

Hydroquinone Mono β-Bromoethyl Ether, $BrC_2H_4OC_6H_4OH$.—A mixture of 22 g. of hydroquinone (0.2 mole) and 45 g. of ethylene dibromide (0.25 mole) was dissolved in a solution of 11.2 g. of potassium hydroxide (0.2 mole) in 150 cc. of methyl alcohol. The mixture was stirred and refluxed for five hours. The potassium bromide was removed, most of the alcohol distilled off and the residue poured into 500 cc. of water. The precipitate was stirred vigorously with cold benzene (150 cc.), which dissolved the mono- and dibromoethyl ethers but not the unchanged hydroquinone nor the bis-ether. (The bis compound, previously prepared by Vorländer,[6] was isolated from the residue.) The benzene solution was washed thoroughly with 8% aqueous sodium hydroxide (100 cc.) in order to separate the mono-ether from the di-ether. The aqueous layer was partly neutralized with hydrochloric acid, filtered with charcoal and acidified. The precipitate (7.0 g.) was purified by recrystallizing from a mixture of benzene and ligroin, from which it separated as faintly yellow, glistening plates, m. p. 107° (corr.). It is soluble in alcohol, ether, acetone, chloroform, benzene, acetic acid and n-butyl alcohol, moderately soluble in methyl alcohol and carbon tetrachloride and slightly soluble in petroleum ether and water.

Anal. Calcd. for $C_8H_9O_2Br$: Br, **36.83.** Found: Br, 37.01, 36.64.

Hydroquinone Di-β-bromoethyl Ether, *p*-$(BrC_2H_4O)_2C_6H_4$.—The benzene solution obtained in the foregoing, from which the mono ether had been extracted with sodium hydroxide, was dried over sodium sulfate and evaporated to dryness. The residue (2.5 g.) was recrystallized from benzene containing a little ligroin from which it separated as slightly yellow, shiny plates, m. p. 115° (corr.). This di-ether is soluble in alcohol, benzene, acetone, chloroform and insoluble in water.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: Br, 49.35. Found: Br, 49.33, 49.27.

Ethylene Glycol Bis-(*m*-hydroxyphenyl) Ether $(HOC_6H_4OCH_2\text{-})_2$.—To a solution of 11.2 g. of potassium hydroxide (0.2 mole) in 150 cc. of water was added 22 g. of resorcinol (0.2 mole) and 60 g. of ethylene dibromide (0.33 mole). The mixture was boiled under reflux with stirring for five hours. The heavy brown oil which formed was separated and treated twice with 50-cc. portions of *5%* sodium hydroxide, whereupon moat of it dissolved. The alkaline solution was filtered with charcoal and the filtrate made just acid to Congo red, thereby precipitating an oil and a white solid. After drying, the oil was dissolved by boiling with chloroform and the dry crystals were purified by two recrystallizations from 50% alcohol. The substance crystallizes in white, glistening flakes, m. p. 165° (corr.). It is soluble in alcohol, ether and acetone, but insoluble in benzene, chloroform, water and ligroin.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.8; H, 5.5.

The oil obtained by chloroform extraction of the crude bis-ether decomposed when subjected to a vacuum distillation.

The ethers described in Table I were prepared in a similar manner by the use of methyl alcoholic potassium hydroxide.

TABLE I

	M. p. (corr.), °C.	Halogen, Calcd.	Found I	Found II
p-$BrC_2H_4OC_6H_4OOCCH_3$	[a] 76.5–77	30.86	30.92	30.94
p-$BrC_2H_4OC_6H_4OOCC_6H_5$	[b] 119	24.90	24.79	24.90
p-$BrCH_2CH_2OC_6H_4OCH_3$	[c] 49–50	34.59	34.79	34.59
$BrCH_2CH_2OC_6H_3$-2-OCH_3-4-$CH{=}CHCH_3$	[d] B. p. 190° (12 mm.)	29.48	29.43	29.32
$BrCH_2CH_2OC_6H_3$-2-OCH_3-4-$CH_2CH{=}CH_2$	[e] 23° (uncorr.) B. p. 182° (13 mm.)	Characterized by trimethylamine addition product. See Table II		
(p-$CH_3OC_6H_4CH_2$-$)_2$	[f] 147.5°	Calcd.: C, 70.0; H, 6.6 Found: C, 69.6; H, 6.8		

[a] Diamond-shaped plates from butyl alcohol. [b] Fine needles from 95% alcohol. [c] The product was freed from the bis compound by dissolving in cold acetone and from the phenol by repeated washing of its benzene solution with aqueous sodium hydroxide. It separated from 80% alcohol in shiny plates having an odor suggestive of licorice. Yield of purified product, 20%. [d] The oil has a peculiar sweetish odor. [e] Colorless oil obtained in 22% yield having a slight odor resembling eugenol. [f] The residue from the cold acetone extraction in (c) was purified by recrystallizing from hot acetone. It separates as white plates, which are soluble in alcohol, acetic acid, hot water, hot acetone and nearly insoluble in benzene.

Aryl Choline Ethers.—These choline ethers were prepared by condensing the β-bromoethyl aryl ethers with trimethylamine, usually in toluene. The rate at which this condensation took place varied considerably with the particular compound. Where there was a tendency for the elimination of the hydrohalide with a formation of trimethylammonium halide, it was found that this secondary reaction could be diminished and sometimes prevented by carrying out the condensation at ordinary temperatures. At this lower temperature, however, the reaction is frequently very slow, requiring a number of days. In work with these materials, as one of us has already found with a number of other halogen derivatives, the first material crystallizing out sometimes contained a greater amount of the products of the secondary reaction, in these cases, trimethylammonium halide. It was found, therefore, desirable in certain instances to cool the reaction mixture to 0° after the reaction had been allowed to go on for a time, and then decant from the crystals formed into another pressure bottle and allow the reaction to proceed. It seems worth while to call attention to this phenomenon since it has happened frequently when definite tests had been

TABLE II

CHOLINE ETHER BROMIDES

Formulas		M. p. (corr.) °C.	Solubility alcohol	Solvent	Crystal form	Halogen, % Calcd.	Found	
p-$HOC_6H_4OC_2H_4N(CH_3)_3Br$	[a]	254	S. sol.	Abs. alc.	Needles	28.94	28.89	28.77
p-$CH_3OC_6H_4OC_2H_4N(CH_3)_3Br$	[b]	144	V. sol.	Hot acet.	Plates	27.55	27.52	27.57
o-$CH_3OC_6H_4OC_2H_4N(CH_3)_3Br$	[c]	139	V. sol.	Acet.	Short needles	27.55	27.72	27.65
p-$C_6H_5COOC_6H_4OC_2H_4N(CH_3)_3Br$	[d]	208–209	Sol.	Alc. eth.	....	21.02	21.16	21.14
p-$CH_3COOC_6H_4OC_2H_4N(CH_3)_3Br$	[e]	152	Sol.	......	....	25.13	25.17	25.23
p-$H_2NC_6H_4OC_2H_4N(CH_3)_3Br$	[f]	195	Sol.	n-Butyl alc.	Triangular needles	29.05	28.96	28.90
p-$CH_3CONHC_6H_4OC_2H_4N(CH_3)_3Br$	[g]	248	S. sol. abs. alc.	Methyl.-ethyl alc.	Fine needles	25.20	25.15	25.23
2-CH_3O-4-$CH_2{=}CHCH_2C_6H_3OC_2H_4N(CH_3)_3Br$		147	Sol.	Alc. eth.	Leaflets	24.21	24.27	24.34
2-CH_3O-4-$CH_3CH{=}CHC_6H_4OC_2H_4N(CH_3)_3Br$		158	Sol.	Alc. eth.	Fine needles	24.21	24.41	24.29

[a] This condensation was brought about at room temperature during several weeks. [b] This reaction required two weeks at room temperature for completion. [c] The reaction required several days for completion at room temperature. The crystals began to form after two hours. They were impure and the product formed after twelve hours was removed and the reactants returned to the pressure bottle. The product formed subsequently was substantially pure. [d] This reaction was substantially complete after three hours of heating at 70°. [e] The reaction was substantially complete after ten days at room temperature. [f] This condensation seemed to be complete after two days at ordinary temperatures. Due to the strong colorations of solutions of this compound with iron salts, the Volhard method could not be used. It was analyzed by the Robertson procedure. The hydrochloride was obtained as feather-like crystals, m. p. 265° (corr.). [g] This reaction was complete in about a week at ordinary temperatures.

made to prove the absence of free halogen acids in the sample of halogen compound used. These substances were all soluble in water and insoluble in benzene, ligroin and ether. Their solubility in acetone and chloroform varied considerably.

Summary

Several aryl substituted β-bromoethyl phenyl ethers have been prepared including the mono derivative of hydroquinone. These halogen compounds have been converted into substituted phenyl ethers of choline. All of them were less active than the unsubstituted phenyl ether in stimulating respiration and blood pressure.

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The Dehydration and Rearrangement of Certain Pinacolyl Alcohols and Related Compounds

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The dehydration and rearrangement of pinacolyl alcohols have been studied in only four cases in which all the groups involved are aliphatic, namely, pinacolyl alcohol itself (*tert*-butylmethylcarbinol),[2] *tert*-butylethylcarbinol,[3,4] tert-amylmethylcarbinol[4] and *tert*-butylisopropylcarbinol.[5] With only the first of these substances has anything approaching a complete study been made. The present investigation was undertaken in connection with theoretical studies on the mechanism of rearrangements.[6] The pinacolyl alcohols selected were 6,6-dimethyldecanol-5 (I) and 3-methyl-3-butylheptanol-2 (II) because of their availability and the variety of courses which their rearrangements might follow. These were prepared by reducing the pinacolones obtained by Meerwein[7] from the rearrangement of the glycol made from butylmagnesium bromide and ethyl α-hydroxyisobutyrate. In order to conserve the pinacolones, the methods of reducing ketones, of dehydrating secondary alcohols and of ozonizing

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(2) Couturier, *Ann. chim. phys.*, [6] *26*, 433–501 (1892): Zelinsky and Zelikow, *Ber.*, **34**, 3250 (1901); Delacre, *Mem. acad. roy. Belg.*, 296 (1904); *Bull. soc. chim.*, [4] *1*, 575, 978 (1907); Nybergh, Hyllningsskrift tillagnad Ossian Aschan, 98–102 (1920); Van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921); Fomin and Sochanski, Ber., 46, 244 (1913); H. S. Rothrock and P. L. Mennier, unpublished results from this Laboratory.

(3) Faworsky and Alexejewa, J. *Russ. Phys.-Chem. Soc.*, *60*, 657–70 (1918).

(4) Edgar, Calingaert and Marker, THIS JOURNAL, 61, 1483 (1929).

(5) Whitmore and Houk, *ibid.*, 64, 3714 (1932).

(6) Whitmore, *ibid.*, **54**, 3274 (1932).

(7) Meerwein. *Ann.*, 419, 121–75 (1919).

olefins were studied with related compounds which were available in larger amounts.

By applying the principles which have been found to hold in related rearrangements,[6] the products which might be formed by dehydrating the pinacolyl alcohols may be predicted. 6,6-Dimethyldecanol-5 (I) might give (a) without rearrangement, 6,6-dimethyldecene-4 (III); (b) with rearrangement of methyl, 2-butyl-3-methylheptene-1 (IV), 5,6-dimethyldecene-4 (V) and 5,6-dimethyldecene-5 (VI); (c) with rearrangement of butyl, 2-methyl-3-butylheptene-i (VII) and 2-methyl-3-butylheptene-2 (VIII). Similarly 3-methyl-3-butylheptanol-2 (II) might give (a) without rearrangement, 3-methyl-3-butylheptene-1 (IX); (b) with rearrangement of methyl, VIII and 2-methyl-3-butylheptene-3 (X); (c) with rearrangement of butyl, IV, V and VI. Both alcohols gave the same olefins, namely, 5,6-dimethyldecene-4 (V), 5,6-dimethyldecene-5 (VI), and 2-methyl-3-butylheptene-2 (VIII). Relatively more of V and VI were obtained from II than from I, indicating the greater mobility of the butyl group. No test for formaldehyde was obtained with any of the ozonolysis products, thus proving the absence of IV, VII and IX and indicating the difficulty in the loss of hydrogen from a methyl group when larger groups are available even though rearrangement is necessary to give an olefin without a terminal methylene group.[8] Butyldimethylacetaldehyde, the ozonolysis product characteristic of III, was carefully sought for. Neither it nor the corresponding acid could be found. Thus neither alcohol gave a detectable amount of normal dehydration without rearrangement.

The only unsatisfactory part of the study is that involving the presence or absence of X. Although its characteristic ozonolysis product, 2-methylheptanone-3, could not be identified by a solid derivative, its properties are so nearly like those of its isomer, 3-methylheptanone-2 obtained from V that this failure is not necessarily significant. Moreover, the dehydration of the related substance 2-methyl-3-butylheptanol-3 gave VIII and X. The latter gave 2-methylheptanone-3 which was identified as the semicarbazone without trouble.

Experimental

Preparation of the Pinacolones.—*n*-Butyl bromide was prepared in 24-mole runs by slight modification of the sodium bromide method of Kamm and Marvel.[9] The mixture was refluxed for eight hours. Stirring was continued through the distillation of the bromide from the reaction mixture. The sulfuric acid washings on dilution with a large amount of water gave 440 g. of the bromide. The total yield of n-butyl bromide, b. p. 98–100" (735 mm.), was 2930 *g.* (89% of the theoretical amount).

n-Butylmagnesium bromide was prepared in 8-mole runs with yields of 90–92%.

Commercial ethyl a-hydroxyisobutyrate was dried with sodium sulfate and distilled through a 40 × 1.5 cm. packed, insulated, total condensation, adjustable take-off

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[8] This agrees with a large mass of unpublished data accumulated in this Laboratory.

[9] "Organic Syntheses," 1921, Vol. I, p. 6.

column,[10] using a 5:1 reflux ratio. The fraction of b. p. 144–145.5° (730 mm.) was used for the preparation of **2-methyl-3-butylheptandiol-2,3** according to the method of Meerwein.[7] The ester in 2-mole lots was added to the Grignard solution from 8 moles of n-butyl bromide using a total of 3 liters of ether per run. After removal of ether, the product was distilled at 2 mm. pressure and divided into fractions below and above 50°. The lower fraction was distilled through the 40 X 1.5 cm. column at 730 mm., giving fractions: (1) below 115°, 7 g.; (2) 115–122°, 15 g. (n-butyl alcohol, identified by the 3,5-dinitrobenzoate); (3) 122–140°, 9 g.; (4) 140–148°, 21 g. (unchanged α-hydroxyisobutyrate, identified by conversion to the solid acid); (5) 148–183°, 10 g.; (6) 183–188°, 10 g. (reacted instantly with bromine in carbon tetrachloride). The material boiling above 50° (2 mm.) could not be distilled through a packed column because of its high viscosity. It was distilled through a 40 X 2.4 cm. column without packing except a layer of beads at the bottom. Otherwise the arrangement of the column was as usual. A reflux ratio of over 5:1 and a pressure of 1 mm. were used. The fractions were: (1) 50–80°, 11 g.; (2) 80–85°, 29 g.; (3) 85–94', 24 g.; (4) 94–99°, 7 g.; (5) 99–104°, 159 g. Fractions 2 4 contained mixtures of the desired glycol and the by-product identified by Meerwein as 2-methylheptanediol-2,3.[7] Fraction 5 solidified in long waxy needles, m. p. 31.5–32" (Meerwein 32°); yield 45%, based on the ester not recovered. A total of 1314 g. of the glycol-2-methyl-3-butylheptanediol-2,3was prepared.

Meerwein's method of rearranging the glycol was slightly modified by lowering the temperature of the sulfuric acid by means of solid carbon dioxide (Dry Ice). The glycol and a mortar and pestle were cooled to 0°. At this temperature the glycol could be finely powdered. A half mole of the glycol was then added over half an hour to 1 kg. of concd. sulfuric acid kept at −20° by the addition of pieces of Dry Ice. Stirring was continued for two hours and then the orange colored reaction mixture was kept in the refrigerator for ten hours. The mixture (then at −2°) was poured on 1.5 kg. of finely cracked ice. The oil layer was separated and the acid layer was extracted with ether. The product was distilled under reduced pressure, b. p. 76–82° (4 mm.), 97–107° (15 mm.). The yield was 63 g. (69%). The other fractions were: (1) below 97° (15 mm.), 6 g.; (3) 107–140° (15 mm.), 3 g.; (4) residue 17 g. Using dilute sulfuric acid kept at −10° instead of ice for diluting the reaction mixture did not increase the yield. A total of 626 g. of the mixture of pinacolones was prepared.

The pinacolones were separated according to the procedure outlined by Meerwein, the details of which were worked out as indicated in the following typical run. To 184 g. (1 mole) of the pinacolone mixture, containing about 35% of the methyl ketone, were added a solution of 40 g. (0.36 mole) of semicarbazide hydrochloride in 100 cc. of water and a solution of 50 g. (0.36 mole) of sodium acetate crystals in 500 cc. of 95% alcohol. After cooling for twenty hours in the refrigerator, a considerable crop of crystals of the semicarbazone of the methyl ketone (3-methyl-3-butylheptanone-2) separated. After stirring and standing six hours more, the crystals were removed by filtration and the mother liquor was diluted to 2 liters with water to precipitate the unreacted ketone, mainly the butyl ketone (6,6-dimethyldecanone-5). On standing for twenty-four hours longer at 0°, more crystals of the semicarbazone of the methyl ketone separated and were removed. The unreacted pinacolone from six runs was treated with semicarbazide as before and allowed to stand a month. More of the crystalline semicarbazone of the methyl ketone separated. The entire process was repeated once more to give only a small amount of crystals.

The semicarbazone of 3-methyl-3-butylheptanone-2 after four crystallizations from 95% alcohol melted at 105–107°. It was better purified by two crystallizations from 60–80° ligroin. The m. p. was 107.2–107.7" (corr.) and was not raised by further crystallizations. A total of 299 g. of semicarbazone of this purity was obtained. The

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[10] Whitmore and Lux, THIS JOURNAL., 54, 3451 (1932)

methyl ketone was regenerated by refluxing half mole portions of the semicarbazone with ten weights of 20% oxalic acid solution for four hours. The yield was 88 g. (96%). Distillation of the products from several runs through a 30 X 0.7 cm. indented column using a reflux ratio of 10:1 gave 206 g. of 3-methyl-3-butylheptanone-2 of b. p. 104.5–105.5" (14 mm.), 70–71° (2 mm.), $n_{\rm D}^{20}$ 1.4371. Meerwein gives b. p. 107.5–108.5° (14 mm.), and $n_{\rm D}^{20}$ 1.43667.

The butyl ketone was recovered from the mother liquors, which gave no further crystallization of the semicarbazone of the methyl ketone. Dilution of the solution with water, separation and drying of the oily layer gave 313 g. of material. Of this only 200 g. distilled. The residue was a tarry material of ammoniacal odor. This proved to be impure semicarbazone of the butyl ketone. Treatment with oxalic acid solution gave a 78% recovery of the butyl ketone from the tar. All the butyl ketone was distilled through the 30 X 0.7 cm. column giving 206 g. of 6,G-dimethyldecanone-5, b. p. 63.0–63.5° (1.5 mm.), 216–217" (735 mm.), $n_{\rm D}^{20}$ 1.4346. Meerwein gives b. p. 105.5–106.5" (14 mm.) and $n_{\rm D}^{20}$ 1.43420.

The 2-methylheptanediol-2,3 obtained as a by-product in the preparation of the main glycol was rearranged by concentrated sulfuric acid at −5°. From 284 g. of crude material boiling at 80–99° (1 mm.) was obtained 123 g. of 2-methylheptanone-3 boiling at 155–156° (728 mm.).

Reduction of the Pinacolones.—Preliminary experiments on various methods of reduction were tried with less expensive ketones.

Platinum oxide catalyst was prepared according to the method of Adams and Shriner and successfully tested in the reduction of maleic acid in a Burgess–Parr hydrogenation apparatus according to the method of Adams and Voorhees. Acetone was hydrogenated with this catalyst to give an 80% yield of isopropyl alcohol, b. p. 79–82" (732 mm.). All attempts to reduce the following ketones with this platinum oxide catalyst gave only unchanged material: methyl isopropyl ketone, methyl n-amyl ketone, 2-methylheptanone-3 and the pinacolone, 3-methyl-3-butylheptanone-2.

Reduction of the first three of these ketones by sodium and moist ether, moist benzene and various dilutions of ethyl alcohol with water gave yields of the carbinols up to 65%. When the best conditions were used with the pinacolones further refinements were introduced which increased the yields. A typical run follows.

To 46 g. (0.25 mole) of 6,6-dimethyldecanone-5 in a 500-cc. three-necked flask fitted with a special mercury-scaled stirrer and a reflux condenser were added 150 cc. of a solution of sodium carbonate saturated at room temperature and 150 cc. of benzene. The stirrer, of the propellor type with highly pitched blades, extended just below the surface of the benzene and was run at a rate slow enough to avoid much disturbance of the sodium carbonate solution. Over a period of thirty-six to forty-eight hours 30 g. (1.3 moles) of sodium was added in small portions in 1–2 mm. cubes. The pieces of sodium floated on the sodium carbonate layer. At the end of the time, 50 cc. of water was added to dissolve solid sodium carbonate which had separated and to react with the last of the sodium. The benzene layer was distilled through a 60 X 1.4 cm. packed adiabatic column using a reflux ratio of 1:1 until the boiling point reached 82° (733 mm.). The residue was distilled under reduced pressure through the same column using a reflux ratio of 5:1. The yield of 6,6-dimethyldecanol-5 of b. p. 112–113° (15 mm.) was 90%. The ketone was reduced in six runs, the fore-run from each distillation being added to the next reduction. A total of 174 g. of the alcohol was prepared. It had the following properties: $n_{\rm D}^{20}$ 1.4469; d_4^{20} 0.845.

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.3; H, 14.1. Found: C, 77.4; H, 14.1.

In an exactly similar way 3-methyl-3-butylheptanone-2 was reduced to give 180 g. of 3-methyl-3-butylheptanol-2, b. p. 112.0–112.5° (14 mm.), $n_{\rm D}^{20}$ 1.4492, d_4^{20} 0.850.

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.3; H, 14.1. Found: C, 77.6; H, 14.0.

Dehydration of the **Pinacolyl** Alcohols.—Again preliminary experiments were tried on less expensive carbinols. Since the literature is definitely lacking on the dehydration of alcohols these experiments will be given in some detail.

n-Butylisopropylcarbinol (24 g.), b. p. 159–164" (740 mm.), was heated with pure p-toluene sulfonic acid (0.5 g.) at 150" for two hours without the formation of any olefin. The addition of a trace of phenol and heating for two hours more gave no change. Finally the mixture was refluxed (162°) for two hours. The original carbinol was recovered unchanged. When 20 g. of the recovered carbinol was refluxed for two hours with a solution of 15 cc. of concd. sulfuric acid in 25 cc. of water, 8.5 g. of olefin, b. p. 125–140" (739 mm.), was obtained.

Capryl alcohol was treated with various concentrations of 100% sulfuric acid in glacial acetic acid at various temperatures. At lower temperatures there was no reaction. At higher temperatures small amounts of olefin and large amounts of capryl acetate were obtained.

Experiments with solutions of 100% sulfuric acid in diethyl ether were more successful, giving as high as 50% yields of olefin.

Finally nineteen runs were made with capryl alcohol and 100% sulfuric acid in varying amounts and under widely varied conditions.[11] The best run follows. To 130 g. of capryl alcohol (b. p. 177.2–177.4" (740 mm.), n^{20}_{D} 1.4260), in a 250-cc. flask connected to a 60 × 1.4 cm. packed adiabatic column set for vacuum distillation was added 5 cc. of 100% sulfuric acid. The mixture was heated to boiling and distilled at atmospheric pressure for eight minutes. The pressure was then gradually reduced to 50 mm. while the remainder distilled. The total time was twenty-five minutes and the highest temperature at the head of the column was 92". A 90% yield of olefin of b. p. 122–128° (733 mm.) was obtained.

Similar experiments were made with dicapryl alcohol, 7-methylpentadecanol-9, (b. p. 130–132° (2 mm.), 102–104° (0.25 mm., McLeod gage), n^{20}_{D} 1.4478). With 25 and 50% solutions of 100% sulfuric acid in glacial acetic acid, 60% yields of olefins were obtained. Nine runs were made with dicapryl alcohol and small amounts of sulfuric acid. The best of these follows. To 54.3 g. of dicapryl alcohol in a flask attached to a 10 X 1 cm. packed column was added 1.3 cc. of 100% sulfuric acid. The mixture was heated for five minutes at a gradually decreased pressure of 500–100 mm. The few cc. of distillate was returned to the flask, the whole washed with sodium carbonate solution and water, dried by heating under reduced pressure and distilled through the 30 X 0.7 cm. column (McLeod gage). A yield of 45.7 g. of olefin of b. p. 106–111° (4 mm.) and n^{20}_{D} 1.4419 corresponding to 91% was obtained. This procedure was repeated with a yield of 90%.

6,6-Dimethyldecanol-5 was dehydrated in the same way as the dicapryl alcohol. This was done in five runs, each using 55 g. of the alcohol and 2 cc. of 100% sulfuric acid. The pressure was reduced to 400 mm. and the mixture was heated as rapidly as possible with a free flame. In seven minutes 4 cc. of water and 10 cc. of olefin distilled, the distillation temperature reaching 140". The reaction mixture was cooled at once, mixed with the distillate, washed with 20 cc. of sodium carbonate solution saturated at 25°, separated, dried by warming under reduced pressure and distilled through the 30 X 0.7 cm. column without reflux. The yield was 46.6 g. of olefin of b. p. 78–83" (14 mm.), and n^{20}_{D} 1.4370, corresponding to 93%. A residue of 2.9 g. was added to the next run for dehydration. In this way 183 g. of the alcohol gave 135 g. of olefin representing a yield of 82%.

3-Methyl-3-butylheptanol-2 was dehydrated in an exactly similar way in three

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(11) *Cf.* Senderens, *Compr. rend.*, **154,** 777 (1913).

runs. In this way 167 g. of the alcohol gave 141 g. of olefin of b. p. 80–85° (15 mm.) and n^{20}_{D} 1.4374 corresponding to a 93% yield.

The Structure of the **Olefins.**—The technique of ozonolysis and identification of the resulting products was developed with the olefins from the dehydration of dicapryl alcohol and of 5-isopropylnonanol-5. The latter was prepared in 69% yield from ethyl isobutyrate and n-butylmagnesium bromide. Properties: b. p. 75.0–75 5° (2 mm.), 110–113" (16 mm.), n^{20}_{D} 1.4446, d^{20}_{4} 0.844.

Anal. Calcd. for $C_{12}H_{26}O$; C, 77.3; H, 14.1. Found: C, 77.4; H, 14.0.

The olefin mixture from dicapryl alcohol on ozonolysis[12] gave definite indications of hexaldehyde, heptaldehyde and 2-methyloctanal [13]

The dehydration of 5-isopropylnonanol-5 with a trace of sulfuric acid or iodine gave 90% yields of olefins (b. p. 190–195° (732 mm.), n^{20}_{D} 1.4376). Ozonized oxygen was passed for thirty-two hours into a solution of 33.6 g. (0.2 mole) of these olefins in 200 cc. of petroleum ether (b. p. 5–30")." The solvent was then removed at 35° and 25 mm. pressure; yield of crude ozonide 96%. This was decomposed with boiling water and zinc dust.[12] A trap containing alcohol kept below 0° was connected with the apparatus. When the first part of the aqueous distillate was redistilled and the first portion treated with benzaldehyde and alcoholic sodium hydroxide,[15] dibenzylidene acetone, m. p. 110–111°, was formed. Extraction of the reaction mixture with ether gave 29 g. of carbonyl compounds, a yield of 76%. Two distillations through the 30 X 0.7 cm. column using a reflux ratio of about 10:1 gave eight fractions of b. p. 48 to 200" and n^{20}_{D} 1.4119 to 1.4237. The 65–75" fraction gave the 2,4-dinitrophenylhydrazone of butyraldehyde, m. p. 122". The 153–158" fraction gave the semicarbazone of 2-methylheptanone-3, m. p. 109°. The 183–188° fraction gave the semicarbazone of nonanone-5, m. p. 89–89.5°. These were all confirmed by mixed melting point determinations. No other products were identified. The dehydration of 5-isopropylnonanol-5 thus gives two olefins, 2-methyl-3-butylheptene-2 and 5-isopropylnonene-4 hydrogen being supplied by both the isopropyl and butyl groups. The amounts of the various carbonyl compounds obtained indicates that the former is formed in much the larger amounts.

The olefins from 6,6-dimethyldecanol-5 were ozonized in the same way giving yields of crude ozonides of 94–98%. These were decomposed by zinc and boiling water as before using the special apparatus devised by one of us (K.) for the rapid removal of the products to avoid their oxidation.[12] The ozonolysis products (65 g.) were twice distilled through a 60 × 1.4 cm. packed adiabatic column using a reflux ratio of over 20 : 1. Sixteen fractions and a residue of 7 g. were obtained. Fraction 1 gave dibenzylidene acetone, m. p. 110.5–111.5"; fraction 3, 6.5 g., b. p. 70–75° (741 mm.), n^{20}_{D} 1.3813, and fraction 5, 6.7 g., b. p. 123–127° (741 mm.), n^{20}_{D} 1.4009, gave the 2,4-dinitrophenylhydrazones of n-butyraldehyde, m. p. 121" and of hexanone-2, m. p. 106". Mixed melting point determinations confirmed these substances. Fraction 8, 4.3 g., b. p. 150–155° (741 mm.), n^{20}_{D} 1.4124 gave no semicarbazone even on standing for seventeen days.

Repeated attempts to make a solid derivative from this fraction resulted in only a small amount of the semicarbazone of 3-methylheptanone-2, m. p. 87°,[16] which was obtained in larger amounts from fractions 9–11, 10.4 g., b. p. 155–161°, n^{20}_{D} 1.414; mixed m. p. 87–88'.

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(12) Whitmore and Church, THIS JOURNAL, 54, 3712 (1932).

(13) This work is being continued by J. M. Herndon in this Laboratory

(14) Supplied by The Viking Corporation, Charleston, W. Va.

(15) Straus and Caspari, *Ber.*, 40, 2698 (1907).

(16) Powell [THIS JOURNAL, 46, 2517 (1924)] gives the melting point of this semicarbazone *as* 82° This is evidently in error. 3-Methyl-heptanone-2 was synthesized from ethyl n-butylacetoacetate and methyl iodide in 45% yield. It had b. p. 157–161° (733 mm.) and n^{20}_{D} 1 414. Its semicarbazone was crystallized from absolute ethyl alcohol to constant m. p 87–88'. Anal Calcd. for $C_9H_{19}ON_3$: C, 58.3; H, 10.3. Found C, 58.5; H, 10.5.

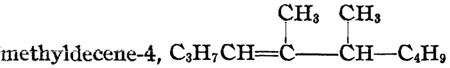
Fractions 14 to 16, 9.1 g., b. p. 178–200°, n^{20}_{D} 1.42, on distillation gave material of b. p. 187–192' and n^{20}_{D} 1.421, which formed the semicarbazone of nonanone-5, as shown by melting point and mixed melting point of 89°.

The material in the cold alcohol trap and the aqueous distillates were tested for formaldehyde using resorcinol and sulfuric acid. No formaldehyde was detected. The test as used gave positive results with known solutions of formaldehyde in the presence of acetone, butyraldehyde and a mixture of the two.

If the dehydration of 6,6-dimethyldecanol-5 had taken place without rearrangement, one of the ozonolysis products of the resulting olefin would be a C_8 aldehyde boiling in the range 130–150°. Fractions 7–9, b. p. 130–157°, were tested for aldehydes with Schiff's reagent with negative results.[17]

The identification of acetone, butyraldehyde, nonanone-5, hexanone-2 and 3-methylheptanone-2 in the ozonolysis products shows that the olefins from the dehydration of 6,6-dimethyldecanol-5 are

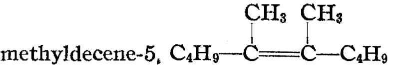
(a) 5,6-dimethyldecene-4,



$$C_3H_7CH{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}H{-}C_4H_9$$

(V)

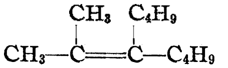
(b) 5,6-dimethyldecene-5,



$$C_4H_9{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}{-}C_4H_9$$

(VI)

(c) 2-methyl-3-butylheptene-2,



$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{C_4H_9}{\overset{|}{C}}{-}C_4H_9$$

(VIII)

The olefins from the dehydration of 3-methyl-3-butylheptanol-2 were ozonized in an exactly similar way. The yields of crude ozonide and crude carbonyl compounds were 96 and 80%, respectively. The careful fractionation of 71 g. of the carbonyl compounds through a 60 X 1.4 cm. column and then through a 60 × 0.7 cm. column of the usual type employed in these researches gave fifteen fractions and a residue of 6.3 g. The water layer from the steam distillation of the ozonolysis product contained acetone. Fraction 3, 3 g., 5–6, 13.5 g., contained butyraldehyde and hexanone-2. Fractions 8–9, 13 *g.*, b. p. 153–158° (733 mm.), n^{20}_{D} 1.413, gave a semicarbazone which melted at 76° even after many crystallizations. The melting points of the semicarbazones of 2-methylheptanone-3 and 3-methylheptanone-2 are 110 and 88°, respectively, the boiling points of the ketones are 155–156° and 157–159° and their refractive indices are 1.412 and 1.414, respectively. Treatment of 16 g. from fractions 7–12 with sodium bisulfite solution failed to give any separation. The material which did not react with the bisulfite was fractionated giving 2 g. of material of b. p. 152–157° (738 mm.) and n^{20}_{D} 1.4120. This gave a small amount of a semicarbazone of m. p. 75°. Three crystallizations from absolute alcohol and three from 50–70° petroleum ether gave a constant melting point of 86–87°. A mixed melting point proved this to be the semicarbazone of 3-methylheptanone-2. Study of the mother liquors from this material failed to indicate the presence of any of the semicarbazone of the isomeric 2-methylheptanone-3.

Fractions 10–11, 9.1 g., b. p. 158–161° (735 mm.), n^{20}_{D} 1.414, also contained 3-methylheptanone-2. Fractions 14–15 on redistillation gave material of b. p. 186–190° (735 mm.) and n^{20}_{D} 1.424 which formed the semicarbazone of nonanone-5.

The water layers and the alcohol trap gave no test for formaldehyde, thus eliminating from consideration all olefins containing a terminal double bond, including the product which would be formed by a normal dehydration without rearrangement.

The identification of n-butyraldehyde and 3-methylheptanone-2 showed the presence of 5,6-dimethyldecene-4. Hexanone-2 indicated 5,6-dimethyldecene-5. These two olefins were formed by the shift of one of the two butyl groups. The formation

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(17) Cf. Conant and Bartlett, THIS JOURNAL, 54, 2896 (1932).

of acetone and nonanone-5 showed the presence of 2-methyl-3-butylheptene-2, formed by the shift of the methyl group. If none of the isomeric substituted heptene-3 was formed (as indicated by the failure to identify any 2-methylheptanone-3), it indicates that the loss of a proton by the rearranged fragment took place exclusively from the tertiary hydrogen and not at all from the butyl group. This would be surprising in that the dehydration of 5-isopropylnonanol-5 gave dehydration involving both the tertiary hydrogen and the butyl group, although mainly the former. This possible inconsistency is being studied further

Summary

1. Meerwein's preparation of 6,6-dimethyldecanone-5 and 3-methyl-3-butylheptanone-2 has been repeated and checked in every detail.

2. A method for reducing complex ketones has been developed and applied to these two pinacolones to give nearly quantitative yields of 6,6-dimethyldecanol-5 and 3-methyl-3-butylheptanol-2.

3. A method for dehydrating secondary alcohols with sulfuric acid has been developed with capryl alcohol and dicapryl alcohol and has been applied to the two pinacolyl alcohols in 2 to give over 90% yields of olefins.

4. The two pinacolyl alcohols in 2 underwent the reversed pinacolone rearrangement, giving mixtures of the same three olefins, 5,6-dimethyldecene-5 and -4 and 2-methyl-3-butylheptene-2. None of the expected 2-methyl-3-butylheptene-3 was detected in the olefins from 3-methyl-3-butylheptanol-2. The structure of the olefins was determined by ozonolysis by a technique developed in this Laboratory.

5. 5-Isopropylnonanol-5 was prepared and dehydrated to give the olefins, 2-methyl-3-butylheptene-2 and -3 as shown by their ozonolysis products.

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Resin Studies. II. A Study and Extension of the Liebermann Color Reaction for Abietic Acid

BY W. A. LA LANDE, JR.

Introduction.—Abietic acid enters into many color reactions, *e. g.*, it gives brilliant colorations with antimony pentachloride,[1] phenol and bromine in carbon tetrachloride solution,[2] methyl or ethyl sulfate[3] and sulfuric acid in the presence of acetic anhydride.[4] Liebermann's test is the most characteristic and is carried out by dissolving a few mg. of the sample in 2–3 cc. of warm acetic anhydride and adding a few drops of concentrated sulfuric acid to the cooled solution. A violet or purplish-red color appears instantly but changes rather quickly through reddish-brown to yellowish-brown. The chemistry of the Liebermann test has not been elucidated. As an approach to this problem there are discussed in this paper the various factors which influence the color production observed in the test, the effect on the colorations of the substitution of other reagents, and the possible structural relationship existing between abietic acid and other compounds of definitely known structure which give the same colorations with the same reagents.

Experimental

Abietic acid was prepared from American "I" wood rosin by Steele's method:[5] acid and saponification no., 185.4; $[\alpha]^{25}_{\mathrm{D}}$ -75.5 (5% in ethyl alcohol); m. p. 158°. Eastman organic reagents were redistilled and used without further purification. Some of the terpenes used in the tests were generously donated by Schimmel and Co.

The Unmodified Liebermann Reaction.—The colors produced when sulfuric acid is added to an acetic anhydride solution of abietic acid depend on the concentration of the solution, the temperature, and the amount of mineral acid added. The following table summarizes the results obtained by adding 0.05 cc. of 95% sulfuric acid to 2 cc. of solutions of the concentrations indicated. The numbers above the arrows show approximately the number of seconds required for the color change.

Concn. of abietic acid	Colorations (25°)
>0.3 *M*	Blue $\xrightarrow{45}$ violet-blue $\xrightarrow{75}$ violet $\longrightarrow$ brown
.2 *M*	Blue $\xrightarrow{17}$ greenish-blue $\xrightarrow{163}$ green-black $\longrightarrow$ brown
.1 *M*	Violet-blue $\xrightarrow{8}$ blue $\xrightarrow{12}$ green $\longrightarrow$ brown
.05 *M*	Purple $\xrightarrow{4}$ violet $\xrightarrow{4}$ green-blue $\xrightarrow{9}$ green $\longrightarrow$ brown
.01 *M*	Reddish-violet $\xrightarrow{25}$ brown-violet $\xrightarrow{30}$ brown

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(1) Steinle and Kahlenberg, *J. Biol. Chem.*, **67**, 425 (1926).

(2) Hicks, *Ind. Eng. Chem.*, **3**, 86 (1911).

(3) Sans, *Ann. chim. anal. appl.*, **14**, 140 (1909).

(4) Liebermann, *Ber.*, **17**, 1884 (1884). Unimportant modifications have been suggested by Storch [*Ber. osteri. Ges. chem. Ind.*, **9**, 93 (1887)]; Morawski [*Chem. Z.*, **12**, 1321 (1888)], and Burchard [Dissertation, Rostock, 18891.

(6) Steele, THIS JOURNAL, **44**, 1333 (1922).

The reaction mixture developed a green or bluish-green fluorescence which was most pronounced in the dilute solutions. At higher temperatures the first color was of shorter duration, *e. g.*, at 100° there was only a momentary flash of the initial color and the intermediate shades did not appear at all. At low temperatures the colors were only slightly less fugitive than at room temperature. Sulfuric acid in excess of a few drops per 2 cc. of abietic acid solution renders the test less delicate due to side reactions and the heat produced on mixing acetic anhydride and the mineral acid. This latter effect can be avoided by dissolving the anhydride in the sulfuric acid before adding it to the abietic acid solution. Practically any concentration of sulfuric acid can be used for the test since the anhydride dehydrates the dilute acid. The colorations are also produced by adding acetic anhydride and sulfuric acid to a solution of abietic acid in an inert solvent. Burchard[4] used chloroform but other polyhalides, alkyl halides, hydrocarbons and carboxylic acids can also be used. The reaction products separated as a tar from those solvents in which sulfuric acid is insoluble. It was not possible to extract the colored intermediates by any of the great number of solvents tried. The colorations were instantly destroyed by water.

The Test with Reagents Other than Acetic Anhydride and Sulfuric Acid.—The anhydrides propionic to heptanoic, and also lauric, and chloroacetic, succinic, benzoic, phthalic and maleic anhydrides were substituted for the acetic anhydride. The colorations produced on addition of sulfuric acid to these solutions[6] were practically the same as those obtained with acetic anhydride solutions.

On addition of 0.05 cc. of sulfuric acid to 2 cc. of 0.3 M solutions of abietic acid in the acyl chlorides acetyl to heptanoyl, and also lauroyl, the following series of colors was obtained: greenish-brown → purplish-blue or blue → purple. The purple slowly passed to brown or reddish-brown. With the acyl chlorides the color changes occurred more slowly than with the anhydrides. Acyl chloride solutions of abietic acid darken on standing. The anhydride solutions remain colorless for months. With benzoyl chloride a strikingly brilliant series of colors was produced: greenish-brown → greenish-blue → indigo-blue → purple. The final color was a dull brown. Benzoyl chloride should replace acetic anhydride in the Liebermann reaction for abietic acid.

Solutions of abietic acid in acetamide and propionamide yielded pink to dark red colors on treatment with sulfuric acid. No characteristic colorations were obtained with benzene sulfonyl chloride as the solvent.

Solutions of abietic acid in the ethyl esters of the acids acetic to lauric were colored pale yellow by the addition of sulfuric acid. The color slowly darkened to a bright strawberry-red which was stable for several minutes. Alkyl halides, ethers, alcohols, hydrocarbons, carboxylic acids, ketones, aldehydes, etc., were used as solvents for the abietic acid. Sulfuric acid produced only dull red or brown colors in these solutions.

Although acetic anhydride is replaceable in the Liebermann test by other anhydrides and by acyl chlorides, the function of the sulfuric acid is apparently unique. Solutions of abietic acid in acetic anhydride and in all of the other solvents mentioned above were treated with other concentrated acids and condensing agents. Without exception, either no coloration, or only a red or reddish-brown coloration, was obtained with H_3PO_4, HPO_3, $HClO_4$, P_2O_5, HCl gas, $(C_2H_5)_2SO_4$, $NaHSO_4$, $ZnCl_2$, $AlCl_3$ and anhydrous CH_3COONa.

The roles of the anhydride or acyl halide and the sulfuric acid may be interchanged. With sulfuric acid as solvent for the abietic acid the addition of RCOCl or $(RCO)_2O$ to a freshly prepared solution immediately produced the characteristic colorations at the interface of the two liquids. Under these conditions the colors were exceedingly fugitive and the mixture quickly became reddish-brown. Since the colorations are produced immediately regardless of which reagent is used as the solvent, any reactions preceding

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(6) In the case of the solid anhydrides the sulfuric acid was added to the molten mixture.

the color formation must occur practically instantly on contact of the compounds involved. The few reactions which are known to occur between the compounds entering into the Liebermann test require considerable time for completion and can therefore be of no significance in the color production. It is possible that abietic acid and the anhydride or acyl chloride react to form a molecular compound as rapidly as the abietic acid dissolves. The colorations produced on the addition of sulfuric acid would then depend on the reaction or rearrangement of this molecular compound to form a color producing configuration. Many compounds, e. g., the chalcones, exhibit this phenomenon (halochromism)[7] in the presence of concentrated sulfuric acid, which has been used for comparing the halochromatic properties of a large variety of compounds.[8] To explain the colorations produced by bufonin with the Liebermann reagents, Wieland and Weil assumed that acetic anhydride adds directly to a double bond. This addition product, after rearrangement, reacts with sulfuric acid to form "halochromic ketone sulfates."[9]

Attempts were made to isolate the colored substances formed in the Liebermann reaction and also to determine the fate of the abietic acid in the reaction. It was not possible to stabilize the colored products and the substances isolated were invariably mixtures of unchanged abietic acid and unworkable tarry material. This part of the work is being continued.

The Possible Structural Significance of the Liebermann Test for Abietic Acid.—The Liebermann reagents have been applied to a fairly large number of compounds. Other anhydrides and the acyl chlorides have not been used before in this test. The following list, which includes those compounds producing some coloration when treated in acetic anhydride solution with a few drops of concentrated sulfuric acid, has been compiled from Beilstein and the original literature: 1.4-dihydrobenzene, 1,3-dihydro-2,3-dimethylbenzene, 1,3-dihydro-1,3-dimethylbenzene, 2-isopropenyl-1-methylcyclopentene, 1-(α-methylallyl)-cyclohexene, $\Delta^{1,8(9)}$-*o*-menthadiene, $\Delta^{2,4}$-*p*-menthadiene, 4-isopropenyl-1,2,4-trimethylcyclohexene, 3-(Δ^2-butenyl)-2,4,4-trimethylcyclohexene, 3-(α-hydroxyisopropyl)-2,2-methylcyclopentene, 3(or 4-)-(α-hydroxyisopropyl)-1-(or 2-)-methylcyclopentene, Δ^1-8-*o*-menthenol, 3-(α-hydroxyisopropyl)-1-methylcyclopentanol produce red (or rose, carmine, etc.) colorations. 4-Isopropenyl-3-methylcyclopentene, $\Delta^{3,8(9)}$-*m*-menthadiene, $\Delta^{6,8(9)}$-*m*-menthadiene (?) or isocarvestrene, $\Delta^{4,6}$-*m*-menthadiene, A6-8-m-menthenol, Δ^2-1,2-dimethylcyclohexenol or cantharenol, 1-(α-hydroxyisobutyl)-3-methylcyclohexene, diresorcin (at 100°), ethyldiresorcin, produce violet colorations. $\Delta^{1,8(9)}$-*m*-menthadiene or sylvestrene, carvestrene (dl-sylvestrene), d- and *dl*-$\Delta^{2,8(9)}$-*m*-menthadiene, Δ^1-8-*m*-menthenol, Δ^2-*m*-menthenol, carveprene (Aschan), produce blue colorations. $\Delta^{4,8(9)}$-*o*-menthadiene, A^8-8-o-menthenol, 1,4-dihydro-1,4-diisopropenylbenzene, 3,4-dihydro-1-isopropenylnaphthalene, 3,4-dihydro-1-(α-hydroxyisopropyl)-naphthalene, 1,2,3,4-tetrahydro-1-isopropenylnaphthalene, produce brown, yellow or green colorations.

According to Aschan[10] only structure I produces the blue color. Structure VI (below) symbolizes the only known m-menthadiene with both double bonds in the ring. This compound gives a violet color in the Liebermann test.'' Monocyclic terpenes with the isopropenyl group ortho or para to the methyl group do not give characteristic colorations with the Liebermann reagents. Many other compounds of unknown or incompletely deter-

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(7) Dilthey, Neuhaus and Schommer, *J. prakt. Chem.*, **123**, 235 (1929).

(8) Pfeiffer, "Organische Molekulverbindungen," 2d ed., p. 68.

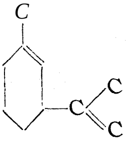
(9) Wieland and Weil, *Ber.*, **46**, 3315 (1913).

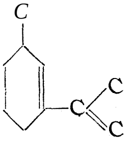
(10) Aschan, "Naphtbenverbindungen, Terpene und Campherarten," 1929, p. 121.

(11) Henderson and Smeaton, *J. Chem. Soc.*, **117**, 144 (1920).

mined structure also give colorations with acetic anhydride and sulfuric acid, *e.* g., cholesterol and some other sterols, certain of the bile acids, bufonin, lupeol, octahydroazulen, certain sesquiterpenes, arnidiol, brein, etc.

The above list is necessarily incomplete, but it is significant that with one important exception (VI), most of the compounds of known structure which give blue or violet colors with acetic anhydride and sulfuric acid are m-menthadienes containing the isopropenyl group and m-menthenols which can give, through dehydration, menthadienes containing this side chain. The location of the second double bond in the ring can vary since all of the following configurations are represented in the compounds giving blue or violet colors


I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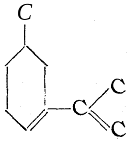
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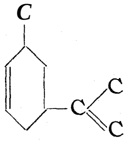
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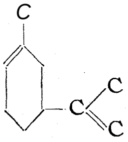
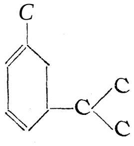

V


VI

It is shown above that pure abietic acid in acetic anhydride solution gives a blue or violet initial color[12] when treated with a little sulfuric acid. This suggests the possibility that abietic acid contains the m-menthadiene configuration which is apparently responsible for the same colorations observed in the test with other compounds of practically certain structure. Derivatively, however, abietic acid is apparently a hydrogenated methyl-retene carboxylic acid, and consequently should contain an isopropyl group. The products obtained by ozonization and permanganate oxidation of the compound include isovaleric acid, isobutyric acid and acetone. The formation of these compounds is obviously most conveniently explained by the presence of an isopropyl group. When abietic acid is heated with sulfur a 17% yield of retene (1-methyl-7-isopropylphenanthrene) is obtained.[13] With selenium a 70% yield of retene is produced.[14] In the temperature range in which these reactions were carried out (250–350") hydrogen selenide decomposes into its elements forming an equilibrium mixture containing only 25% of hydrogen selenide,[15] so that dehydrogenation of the ring system proceeds in a medium which could reduce an unsaturated side chain. At the same temperatures hydrogen sulfide is much less decomposed.

Although L. Ruzicka[16] and others have pointed out that the reactions with sulfur and selenium are drastic ones and not unattended by the possibility of rearrangement or other change, the unaltered retene configuration is retained in most of the structures proposed for abietic acid,

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(12) With abietic acid and probably with many other compounds the intermediate violet or reddish shades are probably mixtures of the initial blue color with the final reddish-brown products.

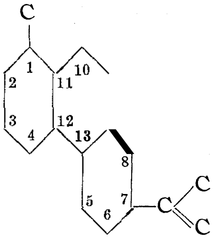
(13) Vesterberg, *Ber.*, 36, 4200 (1903).

(14) Diels and Karstens, *ibid.*, B60, 2323 (1927).

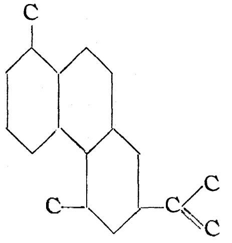
(15) Bodländer, *Z. physik. Chem.*, 29, 429 (1899).

(16) Ruzicka, *Bull. l'inst. pin.*, 59, 115 (1929).

but there is no general agreement on the positions assigned to the second methyl group, the carboxyl group and the two unsaturated linkages.[17] If the isopropyl group in the abietic acid carbon framework is replaced by the isopropenyl group[18] and the second methyl group allocated to a position meta to this side-chain, two structures for the compound are possible:



VII



VIII

By analogy with the menthadiene structures discussed above, the second double bond must be located in the ring to which the isopropenyl group is attached. This bond may have any of the positions indicated in structures I to V (above), excepting the positions between C_{13} and C_{14} and between C_8 and C_{14} in formula VIII. Although two positions are possible for the methyl group, C_5 is the only "free" meta position. However, since this methyl group is eliminated in the reaction with sulfur and selenium, attachment to a quaternary carbon like C_{14} is suggested. It is not intended to infer the structure of a compound, or part of a compound, from the observation of a color test. Considering, however, the uncertain mechanism of the reaction between sulfur or selenium and abietic acid, the conflicting conclusions deducible from the chemical degradation of the compound, and the remarkable specificity of the Liebermann reagents for the $\Delta^{x,8(9)}$-*m*-menthadiene grouping, it is not unreasonable to regard the reaction as a piece of chemical evidence which indicates the possibility of similarity between this latter type of structure and part of the abietic acid molecule.

Summary

A brilliant methylene-blue color is the most characteristic of the colorations produced when sulfuric acid is added to an acetic anhydride solution of abietic acid.

Other anhydrides and acyl chlorides can replace acetic anhydride in the test. Benzoyl chloride gives the most brilliant series of colorations.

On the basis of the Liebermann color reaction for abietic acid it is suggested that abietic acid may contain the $\Delta^{x,8(9)}$-*m*-menthadiene grouping.

PHILADELPHIA, PENNSYLVANIA

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[17] Margosches, Fuchs and Ruzicka, *Chem. Umschau Fette, Öle, Wachse Harze*, **36**, 115 (1929); Ruzicka, Goldberg, Huyser and Seidal, *Helv. Chim. Acta*, **14**, 545 (1931); Rouin, Bull. *l'inst. Pin.*, **59**, 124 (1929); Dubourg, ibid., **59**, 138 (1929); Aschan, *Fenno-Chem.*, 1, 18 (1929).

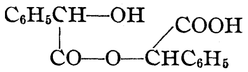
[18] The following construction of the color test leaves the position of the carboxyl group indeterminable, hence it has been omitted from formulas VII and VIII.

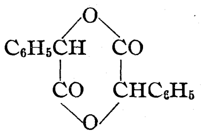
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Mandelic Acid and Related Compounds

BY CHARLES D. HURD AND HARRY R. RATERINK

When a-hydroxy acids are heated they undergo two different types[1] of dehydration: (1) into esters or inner esters (lactide, etc.), and (2) into a cyclic acid anhydride. For mandelic acid to behave analogously there should be formed mandelylmandelic acid (an ester) (I), the inner ester (II) or dimandelic anhydride (III). The esters (I) and (II) were considered by Bischoff and Walden,[2] who pyrolyzed mandelic acid. Other decomposition products which they reported were benzaldehyde, diphenylmaleic anhydride and a gas thought to be carbon monoxide.


(I)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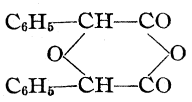
(III)

In the present work with mandelic acid it was established that both types of pyrolysis occur. The fact that residues were formed by heating at 200° for two and six hours which possessed average molecular weights of 380 and 500, respectively, and from which mandelic acid could be regenerated on saponification points to polymers of the recurring unit type

$$C_6H_5—CHOH—CO—O—[—CH(C_6H_5)—CO—O—]_n—CH(C_6H_5)—COOH$$

(mol. wt. = 420 and 554 when $n = 1$ and 2). Undoubtedly some cyclic ester (lactide type) was also present. Almost no gases were formed at 200°.

The depression of the melting point of mandelic acid (118° to 106°) noted by Kizhner[3] when he kept it molten (130°) for several hours may be explained on similar grounds. Some mandelylmandelic acid must have been formed and enough of it persisted through the purification process to lower the melting point. To confirm this reasoning, it was found that the equivalent weight of material similarly prepared (mandelic acid heated for nine hours at 150°, then recrystallized from benzene; m. p. 110°) was 157, not 152.

Anhydride Formation.—At higher temperatures (250°) diphenylmaleic anhydride and phenylacetic acid are important reaction products. Dimandelic anhydride is the only logical forerunner of these substances, the former being produced from it by detachment of the elements of water

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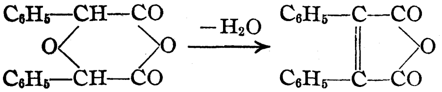
(1) This subject is discussed by Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, New York, 1929, pp. 424–442.

(2) Bischoff and Walden, Ann., **279**, 118 (1894).

(3) Kizhner, *J. Russ. Phys.-Chem. Soc.*, **56**, 15 (1925); *Chem. Abstracts*, **19**, 2940 (1925).



and the latter by detachment of phenylketene which, with water, would give rise to phenylacetic acid: $C_6H_5CH{=}C{=}O + H_2O \longrightarrow C_6H_5CH_2$-COOH. Benzaldehyde is formed concurrently. The phenylacetic acid was discovered in preliminary work with Mr. Fred E. Smith. As a matter of fact, its molar yield exceeded that of diphenylmaleic anhydride so it is surprising that earlier workers made no mention of it. The phenylacetic acid from mandelic acid *via* dimandelic anhydride and phenylketene is strictly analogous to the formation of diphenylacetic acid from benzilic acid[1] *via* "benzilide" and diphenylketene. "Benzilide" should be renamed dibenzilic anhydride.

Dimandelic Anhydride.—In support of this contention, it was found that synthetic dimandelic anhydride pyrolyzed rapidly at 250° into carbon oxides, benzaldehyde, phenylacetic acid, diphenylmaleic anhydride and tar. These were also the products when mandelic acid itself was taken. Less phenylacetic acid was formed as would be expected because of the limited quantity of water available from the anhydride as compared with the acid.

Dimandelic anhydride was synthesized *via* ethyl dimandelate which was prepared as follows: $PhCHONaCOOEt + PhCHBrCOOEt \longrightarrow NaBr + O(CHPh{-}COOEt)_2$. The ester was hydrolyzed to the acid and the acid converted to dimandelic anhydride by heating with acetic anhydride.

It is conjectural whether the intermediate between mandelic acid and dimandelic anhydride is dimandelic acid $O(CHPh{-}COOH)_2$, or mandelic anhydride, $(PhCHOHCO)_2O$. Some evidence for the latter was the formation of mandelanilide by interaction of the neutral residue from a 200°-run with aniline, after demonstrating that no action occurred similarly between ethyl mandelate (an ester) and aniline.

It has been assumed that carbon monoxide predominates in the gas from α-hydroxy acids but from mandelic acid at 250° about equivalent molar amounts of carbon monoxide and carbon dioxide were formed.

Cyclohexylglycolic Acid, $C_6H_{11}CHOHCOOH$.—Structurally, this acid resembles mandelic (or phenylglycolic) acid. Its course of pyrolysis, however, more resembled lactic (methylglycolic) acid. If the electron attraction of R in RCHOHCOOH determines the course of the reaction, this is reasonable, for the order of decreasing electron attraction is phenyl, methyl, cyclohexyl. The chief gas from cyclohexylglycolic acid was carbon monoxide. Hexahydrobenzaldehyde was found but there was no evidence for cyclohexylacetic acid or dicyclohexylmaleic anhydride.

In a preliminary study of dilactic anhydride, these reaction products were identified: carbon monoxide, carbon dioxide, acetaldehyde.

Experimental Part

Procedure.—A weighed quantity of substance was placed in a 25-cc. distilling flask which was connected in series to a condenser, a receiver, a three-way stopcock, a drying tube (sulfuric acid), a bulb for carbon dioxide absorption (30% KOH), another drying tube and three-way stopcock, and finally to a gas collecting bottle. The two stopcocks were connected to each other, shunting the absorbing bulbs, to correct for the excess of expanded gas during cooling. In some experiments the carbon monoxide was determined directly by having the air displaced with carbon dioxide prior to a run and by using carbon dioxide as a sweep. The carbon dioxide was removed by alkali.

Decomposition into Volatile Products.—The essential data concerning experiments with mandelic acid, dimandelic anhydride and cyclohexylglycolic acid are summarized in Table I. Gas began to appear at 210–220° but the bath temperature could be raised quite rapidly to 250°, where it was maintained until gas evolution ceased. Nothing but water and aldehyde was found in the liquid distillate. In the first run with mandelic acid, for example, there was 2.23 g. of distillate and 6.29 g. of residue. The 2.23 g. was shown to contain at least 1.19 g. of benzaldehyde *via* benzaldehyde phenylhydrazone and the weight of water was taken as the difference or 1.04 g.

TABLE I

VOLATILE PRODUCTS OF THE REACTION

Subs. taken, g.	Duration of heating, hours	Products formed				Moles of products formed for each 10 moles of substance taken			
		CO_2, g.	CO, cc.	H_2O, g.	Aldehyde deriv.,[a] g.	CO_2	CO	H_2O	Aldehyde[b]
Mandelic Acid									
10	2.5	0.730	344	1.04	2.20	2.51	2.32	8.8	1.70
10	2.5	.870	336	1.32	2.92	3.00	2.27	11.1	2.26
10	2.5	.750	406	..	..	2.57	2.74	..	..
Dimandelic Anhydride									
5.1	2 0	.236	253	0.15	0.9	2.84	5.95	4.4	2.48
Cyclohexylglycolic Acid									
2.17	0.5	.026	...	..	..	0.4	..	..	..
1.96	0.5	.041	...	..	..	0.7	..	..	..
1.09	2.0	.066	...	.27	.38	2.2	..	21	2.7
0.60	2 0		53.8	..	..	..	6.2	..	..
1.59	2.0	[c]	149	..	..	..	6.7	..	..
1.59	2.5	[c]	116	.27	.39	..	5.2	15	2.2
1.58	2.0	[c]	131	.24	.50	..	5.9	13	2.9

[a] Benzaldehyde phenylhydrazone, m. p. 155°, from mandelic acid or dimandelic anhydride; hexahydrobenzaldehyde semicarbazone, m. p. 172°, from cyclohexylglycolic acid. These were collected in a Gooch crucible and dried at 100° for one hour before weighing. [b] Benzaldehyde or hexahydrobenzaldehyde. [c] Carbon dioxide atmosphere maintained; gas collected over 10% KOH solution

The Residue from Mandelic Acid.—The phenylacetic acid was extracted from the 6.29 g. of residue in the first run with cold 10% sodium hydroxide solution. The solution was acidified, the precipitate collected and crystallized from hot water. The white crystals of phenylacetic acid weighed 1.18 g.; m. p. (and also mixed m. p.), 71–72°.

The more insoluble diphenylmaleic anhydride was extracted by hot 10% sodium hydroxide solution. Acidification gave a red precipitate which was recrystallized from ethyl acetate. The yellow crystals melted at 154–155°; weight, 1.86 g. These weights correspond to **1.32** and **1.13** moles, respectively, of phenylacetic acid and diphenylmaleic anhydride for each ten moles of mandelic acid taken.

The Residue from **Dimandelic** Anhydride.—By extracting this residue similarly with cold and then hot **10%** alkali solution there was isolated **0.38** g. of yellow diphenylmaleic anhydride (m. p. 150–152°) and a small quantity of white phenylacetic acid (m. p. **69–71°).** When the diphenylmaleic anhydride was heated with aniline, it changed to diphenylmaleic phenylimide,[4] of m. p. **170–171°** after crystallization from alcohol.

The Residue from Cyclohexylglycolic Acid.—This was a dark red resin from which nothing was extracted by cold potassium hydroxide solution. Hence, acids were not formed in the pyrolysis. About three-fourths of the residue was soluble in hot 10% potassium hydroxide solution.

Dilactic Anhydride.—A **10.8-g.** portion of this material was passed through a tube in an electrically heated furnace at 550° during one hour. From the effluent vapors, **1.4** g. of acetaldehyde was condensed in a spiral cooled by ice–salt. Its identity was confirmed by the aniline derivative,[5] $CH_3CH(NHC_6H_5)CH_2CH{=}NC_6H_5$, m. p. 126°. The large volume of gas was carbon monoxide and carbon dioxide in about the ratio of **4**:1 by volume.

Mandelic Acid at **150°.—When 15** g. of mandelic acid was heated for nine hours at 150° and **20** mm., **1** g. of water was collected as distillate. The residue was soluble in ether and completely extracted therefrom by a **10%** solution of sodium hydroxide. Acidification of the alkaline extract and crystallization of the precipitate from benzene gave a substance melting at 110°. Its neutral equivalent was **156.7. A** mixed melting point value of 112–114° was obtained with known mandelic acid of m. p. **116**" and of neutral equivalent **152.2** (experimental).

Mandelic Acid at **200°.—Ten-gram** samples were used. In the distillates, **1** g. of water and **0.3** g. of benzaldehyde were identified. The resinous residue (R) from a ten-hour heating at **200" (10** mm. or **760** mm.) contained no mandelic acid, for it was insoluble in sodium carbonate solution. Furthermore, it was much more soluble in benzene than mandelic acid. The latter crystallizes readily from hot benzene on cooling, but (R) did not separate. From hot diamyl ether solution, a nondescript material, m. p. **65–75°,** separated on cooling.

(R) was freed of traces of mandelic acid by stirring for ten minutes with sodium carbonate solution. To some of the residue, aniline was added in excess and the excess was distilled off at ordinary pressure. Mandelanilide, m. p. **146°,** was easily isolated from the non-volatile portion. When ethyl mandelate was treated similarly with aniline, no mandelanilide was isolable.

(R) was soluble in hot 20% sodium hydroxide solution. The 110° crystals were again encountered on acidification and crystallization from benzene.

A **10-g.** portion of **(R),** when pyrolyzed at **250"** as described above, gave (in g.): **C_6H_5CHO, 0.9; H_2O, 0.3; $C_6H_5CH_2COOH$, 0.8;** diphenylmaleic anhydride, **1.7;** CO_2, **0.86;** and **3.64** cc. of CO.

(R) from a two-hour run gave molecular weight values of **370, 390, 360, 390, 397** (average, **381)** by the ebullioscopic method in acetone. (R) from a six and one-half hour run gave values of **529, 492, 492** (average, **504).** The calculated molecular weight of mandelic acid is **152.**

Synthesis of Reagents.—Mandelic acid was synthesized by the method in "Organic Syntheses" (Vol. VI, p. **58).** Cyclohexylglycolic acid was made by the method of Godchot and Frezouls.[6] The melting point of 130° given by these authors was confirmed **but** it differs from the value **(166°)** of Zelinsky and Schwedoff.[7] Hexahydrobenzaldehyde,

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[4] **Anschütz and Bendix, Ann., 259,** 65 (1890), **found the m. p. to be** 174-17Ro

[5] **Eckstein,** ***Ber.*****, 26,** 2030 (1892); **Miller,** ***ibid.*****, 25,** 2072 (1892).

[6] **Godchot and Frezouls,** ***Compt.*** **rend.. 150,** 1248 (1910).

[7] **Zelinsky and Schwedoff, Ber., 41,** 2676 (19081.

which was required for this synthesis, was made in better yields *via* cyclohexylmagnesium chloride and ethyl orthoformate (followed by hydrolysis) than by dehydrogenation of cyclohexylcarbinol.

Ethyl Dimandelate, $O(CHPh-COOC_2H_5)_2$.—The sodium salt of ethyl mandelate was prepared from 7.4 g. of finely cut sodium and 65 g. of ethyl mandelate in 200 cc. of dry ether. Stirring was maintained for seven hours. Then 78 g. of ethyl phenylbromoacetate was added. Considerable heat was evolved. The reaction mixture was left overnight. To work up the products these steps were taken: addition of a carbon dioxide stream; then water to dissolve the sodium bromide; separation, drying and distillation of the ether layer. The unused reactants were taken off up to 170° (22 mm.) and the crude ethyl dimandelate from 170–218° (8 mm.). Redistillation of the latter gave the pure ester, b. p. 215–216° at 8 mm. It was viscid but it would not crystallize; yield, 32 g., or 30% of the theoretical.

Anal. Subs., 0.1754, 0.2158: CO_2, 0.4608, 0.5604; H_2O, 0.1041, 0.1268. Calcd. for $C_{20}H_{22}O_5$: C, 70.1; H, 6.47. Found: C, 71.6, 70.8; H, 6.59, 6.53.

Dimandelic Acid Hydrate, $O(CHPhCOOH)_2 H_2O$.—Ethyl dimandelate was refluxed for five hours with 25 g. of potassium hydroxide and 100 cc. of water. Acidification of the cooled solution threw down a thick, red oil. After washing, it solidified and gave beautiful white crystals after two crystallizations from water. The acid was soluble in ether, alcohol, acetone, ethyl acetate and sparingly soluble in hot benzene; but water was the best crystallizing medium. The yield was 15 g. or 53%.

Anal. Subs., 0.1578: CO_2, 0.3662; H_2O, 0.0761. Calcd. for $C_{16}H_{14}O_5$: C, 67.2; H, 4.90. Calcd. for $C_{16}H_{16}O_6$: C, 63.2; H, 5.31. Found: C, 63.3; H, 5.35. *Neutral Equiv.* Subs., 0.4219: cc. of 0.08806 N alkali, 31.33. Calcd. for $C_{16}H_{16}O_6$: equivalent weight, 152.1. Found: 152.9.

The acid did not melt sharply but softened slowly over a wide range, 120–130°. Apparently dehydration was occurring. Its practical insolubility in cold water delineated it sharply from mandelic acid.

Dimandelic Anhydride.—Five grams of dimandelic acid hydrate was refluxed for a short time with acetic anhydride, some of the solvent removed and the residue cooled. White, needle-like crystals (2.6 g.) of dimandelic anhydride separated and more was obtained later from the filtrate. After drying over potassium hydroxide in a desiccator the solid melted at 152–154°.

Anal. Subs., 0.1810: CO_2, 0.4725; H_2O, 0.0750. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.48. Found: C, 71.2; H, 4.64.

Dilactic Anhydride.—Jungfleisch and Godchot's directions[8] for the synthesis of ethyl diiactate were satisfactory: $NaOCHMeCOOEt + BrCHMeCOOEt \longrightarrow O(CHMeCOOEt)_2 + NaBr$. Their directions for hydrolysis to dilactic acid and thence to the anhydride were inadequate. The trouble was caused by (1) the presence of unhydrolyzed ester, (2) the incomplete anhydrization by vacuum distillation alone. These directions were adopted after considerable search in preliminary experiments.

Ethyl dilactate (48 g.) was refluxed for nine hours with 100 cc. of alcohol and 20 g. of sodium hydroxide, 25 cc. of water being added at the end of three hours. Then the alcohol was distilled off and water added. Any unhydrolyzed ester was removed at this point by ether extraction. Then the aqueous layer was acidified (sulfuric acid), ether extracted and the ether removed. This dilactic acid was refluxed for one-half hour with acetic anhydride. On fractionation, the portion boiling at 125–128° (33 mm.) was collected. It remained liquid. The yield of pure anhydride, based on the total ester taken, was 74%.

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[8] Jungfleisch and Godchot, Compt. *rend.*, 144, 979 (1907); 145, 7 (1907).

Anal. Subs., 0.3356, 0.2838; cc. of 0.1062 *N* alkali, 43.69, 36.73. Calcd. for $C_6H_8O_4$: equivalent weight, 72. **Found:** 72.3, 72.7.

The necessity for the removal of the ester was shown by the high neutral equivalent value of 85 which was obtained when the step was omitted.

Summary

Mandelic acid undergoes an esterification process at 200° or below into PhCHOHCO—O—(CHPhCOO)$_n$—CHPhCOOH but the pyrolysis into diphenylmaleic anhydride and phenylacetic acid at 250° is best explained by assuming the transitional, concurrent existence of dimandelic anhydride. This is similar to the known transformation of benzilic acid into dibenzilic anhydride (benzilide). The other products from mandelic acid at 250° are water, benzaldehyde, carbon dioxide and carbon monoxide.

Ethyl dimandelate, dimandelic acid hydrate and dimandelic anhydride were synthesized. Dimandelic anhydride pyrolyzed at 250° in the manner of mandelic acid. A preliminary study was made of dilactic anhydride.

Cyclohexylglycolic acid decomposed at 250° into carbon monoxide and hexahydrobenzaldehyde, presumably through intermediate esters of the type mentioned with mandelic acid. In contrast to mandelic acid, the yield of carbon dioxide was small and there was no evidence for the formation of acid anhydrides as intermediate products.

EVANSTON, ILLINOIS

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Certain Dichloronaphthalenes and Related Intermediates

BY R. W. BEATTIE[1] AND FRANK C. WHITMORE

Although all of the ten dichloronaphthalenes have long been known, the literature contains a remarkably small amount of information regarding their preparation and properties. The present research was undertaken to produce 50–100 g. samples of 1,2-, 1,4-, 1,5- and 2,6-dichloronaphthalenes in a high state of purity.

The methods recorded in the literature for making the intermediates and the dichloro compounds are given in too little detail to be of any great help in this work. In each case various suggestions obtained from the literature were tested and modified until combinations of real preparative value were developed. The processes evolved represent an unusual amount of laborious experimentation and consequently are recorded in some detail.

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(1) Submitted in partial fufilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

Experimental

Preparation of the Chloronaphthalene Sulfonates.—The starting materials for most of the present work were the following commercial intermediates,[2] all aminonaphthalene sulfonic acids with the groups in the positions indicated. Naphthionic acid (1,4); Laurent's acid (1,5); 1,6-Cleve's acid (1,6); 1,7-Cleve's acid (1,7); Peri acid (1,8); Brönner's acid (2,6); F-acid (2,7); and Badische acid (2,8). These were dissolved in alkali, filtered, precipitated by acid and diazotized by the addition of solid sodium nitrite in the presence of excess hydrochloric acid. Any excess of nitrous acid was destroyed by urea. The suspension of the solid diazonium compounds was added with stirring to an excess of cuprous chloride solution in hydrochloric acid. In the first part of the work the resulting mixture was evaporated to dryness. Since the reactions were carried out in 20-liter quantities, this was laborious and troublesome because of the large amounts of hydrogen chloride evolved. The result was a dry mixture of the desired sodium chloronaphthalene sulfonate with inert sodium and copper salts which could be treated directly with phosphorus pentachloride to make the sulfonyl chloride. It was later found that the addition of large amounts of sodium chloride to the mixture after the Sandmeyer reaction precipitated the sodium chloronaphthalene sulfonate, contaminated only by sodium chloride. This was dried and treated with phosphorus pentachloride. The 1,4- and 2,7-compounds precipitated from the reaction mixtures without the addition of sodium chloride. The others had to be salted out. Typical preparations follow.

Sodium 1-Chloronaphthalene-5-sulfonate (Evaporation Method).—A solution of 440 g. of Laurent's acid in 1 liter of solution containing 80 g. of sodium hydroxide was placed in a 20-liter crock stirred mechanically and treated with 500 cc. of water and 1 kg. of crushed ice, followed by 1 liter of 28% commercial hydrochloric acid. Crushed ice was added when necessary to keep the mixture below 5°. The suspension was stirred and diazotized at 0 to 5° by the addition of 135 g. of powdered sodium nitrite during eight hours. A small amount of urea was added to remove excess nitrous acid. In another 20-liter crock 1 liter of a solution of 2 mols of cuprous chloride in hydrochloric acid was stirred while the diazotized mixture was added to it. A vigorous evolution of nitrogen followed. The mixture was allowed to stand overnight and then evaporated in large dishes on steam-baths with mechanical stirring and the aid of air jets directed across the surface. The solid residue was powdered and dried in an oven at 110–120°. The gray powder obtained weighed 985 g.

Sodium 1-Chloronaphthalene-6-sulfonate (Salting-out Method).—A similar run with 800 g. of 1,6-Cleve's acid was carried through the treatment with cuprous chloride. The solution was then filtered from a small amount of insoluble material and treated with 1.5 kg. of sodium chloride with stirring. The sodium sulfonate precipitated, was filtered off and air-dried to constant weight at 70°; yield 490 g.

Preparation of the Chloronaphthalene Sulfonyl Chlorides.—The nine sulfonyl chlorides of the present study were all made as follows: in a large mortar previously heated on a steam-plate an excess of phosphorus pentachloride was quickly powdered (hood) and ground vigorously with the dry powdered crude sodium sulfonate. Heat was evolved and the mixture became fluid. When the reaction was complete the grinding was stopped and the mixture was allowed to stand overnight. The hard crystalline mass was then broken up and added carefully to an excess of cracked ice. After washing by decantation, the crude sulfonyl chlorides were ground with water in the mortar to remove any unchanged halides of phosphorus. After air drying, the crude sulfone chlorides were extracted in large funnel extractors[3] with boiling ligroin (60–90°). The

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[2] Most of these materials used were supplied by the Dyestuffs Department of E. I. du Pont de Nemours & Co., through its Jackson Laboratory.

[3] "Organic Syntheses," 1922, Vol. II, p. 49.

cooled extract gave crystals which could be further purified by crystallization from ligroin, carbon tetrachloride or glacial acetic acid. The results with the sulfonates and sulfonyl chlorides are summarized in Table I.

TABLE I

PREPARATION OF CHLORONAPHTHALENE SULFONYL CHLORIDES

Intermediate[a]	$ClC_{10}H_6SO_3Na$, g. made	$ClC_{10}H_6SO_2Cl$ Groups	Yield,[c] %	M. p.
Na naphthionate	2473[b]	1,4	70	92–93
Laurent's acid	5215[d]	1,5	30	
Cleve's acid, 1,6	1351"	1,6	60	111–112
Cleve's acid, 1,7	1636"	1,7	45	92–92.5
Peri acid	3937[d,f]	1,8	30	96–98
Peri acid	4085"			
$2\text{-}NH_2C_{10}H_6SO_3Na\text{-}1$	582[g]	2,1	50	74–75
Bronner's acid (68%)	3139[d]	2,6	30	109
F-acid	291[b]	2,7	60	84.5–85
Badische acid	368[e]	2,8	[h]	129

[a] In most cases several runs were made. The weights of intermediates used were nearly equal to the weights of salts obtained. [b] Sodium salt precipitated spontaneously. [c] Yield based on crude salts used. [d] Mixture of Na and Cu salts evaporated to dryness. [e] Na salt precipitated by adding solid sodium chloride with stirring. [f] This salt mixture could not be dried above 100° without some decomposition. This salt could not be dried above 70° without decomposition. [h] The 2,8 sulfonyl chloride was obtained only by heating the crude sodium salt with phosphorus pentachloride at 120–130°.

The following sulfonyl chlorides were similarly prepared: naphthalene-1-sulfonyl chloride, m. p. 65–66.5°, 449 g., 66% yield; naphthalene-2-sulfonyl chloride, m. p. 76–77°, 1315 g., 64% yield; naphthalene-2,7-disulfonyl chloride, m. p. 156–157°, 600 g., 42% yield.

Preparation of the Dichloronaphthalenes.—The preparation of the 1,4 compound is typical. In a 500-cc. flask fitted with a wide reflux condenser 52 g. of 1-chloronaphthalene-4-sulfonyl chloride (1 mol) and 125 g. (3 mols) of phosphorus pentachloride were heated in an oil-bath at 160–165" for five hours. The mixture was cautiously poured on a large amount of cracked ice. The gray liquid solidified when washed with water. The crude solid was ground with water, dried and extracted with 200 cc. of alcohol. The hot extract was treated with decolorizing carbon, filtered and diluted with water to a slight turbidity. On cooling, long white needles separated, m. p. 67–68°, 19 g., 49% yield. A run using 418 g. of the sulfonyl chloride gave 150 g. of 1,4-dichloronaphthalene, m. p. 67.4–68°. In a similar way the following dichloronaphthalenes were prepared: 1,5-, 97 g., m. p. 106–107°, 36% yield; 1,2-, 112 g , b. p. 295–298°, m. p. 33–34', 36% yield; 2,6-, 52 g., m. p. 136°, 45% yield.

Summary

1. The preparation of four of the dichloronaphthalenes and of nine of the chloronaphthalene sulfonyl chlorides has been developed on a large laboratory scale.

STATE COLLEGE, PENNSYLVANIA

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[CONTRIBUTION FROM THE INDUSTRIAL-FARM PRODUCTS DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Composition of the Non-Phenol Portion of Bay Oil[1]

BY S. PALKIN AND P. A. WELLS

The major part of the oil of bay[2] (obtained from the leaves of *Pimenta acris*, or *Bois d'* Inde) consists of phenols, principally eugenol with some chavicol.

The non-phenol portion of the oil has been shown[3] to consist of myrcene, phellandrene, citral and the methyl ethers of eugenol and chavicol. According to Power and Kleber, the reported finding of a-pinene by Mittmann[4] is in error.

In connection with a general survey of the industries of the Virgin Islands, a reinvestigation of this oil was deemed desirable.

In the present investigation use was made of a pressure controlled vacuum-fractionating assembly described later, whereby a more effective separation of the constituents of bay oil than that indicated in previous reports was made possible. Systematic examination of the fractions so obtained shows the oil to be more complex than heretofore believed, and the information in the literature regarding the composition of the oil is in need of revision in several particulars.

The presence of myrcene, citral and phellandrene was confirmed without much difficulty, although the physical properties of myrcene would seem to be somewhat different from those previously reported. Present findings show definitely, however, that the non-phenol portion of the oil contains several constituents not previously stated to be present. These include small quantities of a-pinene, substantial proportions of cineol, and of dipentene (with some limonene), the latter an integral part of the oil. It is presumed that dipentene obtained by Power and Kleber in one of their experiments was regarded by them as an isomerization product of one of the other constituents, since these authors did not include their finding of the dipentene in the summary of constituents.

Methyleugenol and methylchavicol, thought by them to be present in appreciable quantities, if present at all in the true *Pimenta acris* oil, are there only in traces as shown by methoxyl determinations of appropriate fractions. A very small quantity of a geraniol-like alcohol is also present, but its identity was not determined.

Contrary to the belief that only one optically active substance is present in bay oil (a-phellandrene), repeated fractionation shows definitely that there are at least four, three of which are positive and one negative, the

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(1) Presented before the Division of Medicinal Chemistry, Denver Meeting of the American Chemical Society, September 22–26, 1932.

(2) "The Volatile Oils," Gildemeister and Hoffmann, Vol. III, 1922, pp 193–194.

(3) Power and Kleber, *Pharm. Rundschau*, 13, 60 (1895).

(4) Mittmann, *Archiv. Pharm* , 529–548 (1889).

latter sufficiently predominating in effect to give the oil as a whole a negative rotation.

The various constituents found by way of fractionating the *phenol free* portion of the oil were also characterized from appropriate fractions of the *whole bay oil* (the whole oil without preliminary removal of the phenols) when similarly fractionated (data obtained on the latter are not included here). The properties determined on fractions of the whole oil, such as densities, refractive indices and rotations, corroborated previous findings.

Experimental Part

Through the cobperation of Mr. C. L. Horn of the St. Thomas Agricultural Experiment Station and Mr. E. V. Roberts of the Forest Service a 1600-g. sample of authentic bay oil was procured.

The oil was obtained from the fresh green leaves of *Pimenta acris* collected in St. John and prepared by steam distillation in the usual manner, the yield of oil being about 1.22%.

The oil had the following properties: n_D^{20} 1.5134; $d_4^{15.5}$ 0.9796; *a,,* —2.4" (100 mm.); aldehyde as citral (Kleber method), 2.0%; total phenol (by volume), 58.4%.

Separation of the Phenol from the Non-phenol Portion.—It is rather difficult to prepare the non-phenol portion of bay oil entirely free from phenol. In order to effect a complete separation, the following special precautions were taken. The bay oil (1500 g.) was extracted with an excess of 5% sodium hydroxide solution until shown to be phenol free by testing small portions of the alkaline washings with (diazotized) p-nitroaniline.6 (The test is particularly delicate for eugenol.) The non-phenol oil was then thoroughly freed from alkali by washing first with *cold* tenth normal sulfuric acid, and then by a series of successive washings with cold water until the washings were neutral. The alkali phenolate solution was carefully extracted a number of times with ether to effect the recovery of small quantities of non-phenol oil dissolved by the phenolate.

The ethereal extract, after a similar washing, was distilled to remove the ether, the residual oil was again washed with alkali to remove traces of phenol and then with acid, water, etc., as before, and this oil added to the bulk of oil. The total non-phenol oil, after drying over anhydrous sodium sulfate and filtering, weighed 525 g.

In view of the wide difference in boiling points of the constituents, the sample used for the fractionation (500 g.) was given a preliminary distillation under reduced pressure and separated into two fractions of convenient toiling range, the first 342 g. distilling up to 68° at 20 mm. and the remainder distilling above this point. During the fractionation proper the second portion was added when the appropriate distillation temperature (68° at 20 mm.) was reached.

Fractionating Apparatus

A. **Large** Fractionating Assembly.—A wire gauze plate rectifying column (32 plates, 5 cm. inside diameter, 200 cm. in height) which is an improved form of this type of column described by the author in previous publications.6

Thermal insulation for the column was provided by an electrically heated jacket, which was divided into five separate circuits, each rheostat controlled.[7] Thermometers

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(5) Palkin and Wales, THIS JOURNAL, 46, 1488 (1924).

(6) Tech. Bull. 276, U. S. Department of Agriculture; Ind. *Eng. Chcm., 26, 95* (1933).

(7) Bruun, *Bur. Standards* J. *Research, 7,* 851 (1931).

were placed at appropriate intervals in the space between the column and jacket tubes to show temperature gradient.

The superior efficiency of lagged over unlagged columns has been shown by Marshall and Sutherland.[8]

A steel waste-paper basket, with the bottom cut out and lined with asbestos served as a jacket for the distillation flask.

Pressure in the system was maintained constant by means of a short inclined mercury regulator and relay, described in a previous publication.[6] Virtually all the distillations were carried out at 20 mm. or less.

B. Small Fractionating Assembly.—This assembly was in its general plan, including the plate column (20 plates and about 120 cm. in height), like the large one. Details of its construction are given in the earlier publication.[6]

Fractionation.—In general the bulk of the sample was fractionated in the large (32-plate) column and the last 60 to 80 g transferred to the smaller column to complete the fractionation. The fractions so obtained were examined for density refractive index, rotation, etc., and in most instances refractionated twice (in some instances after the removal of citral and cineol), and the physical constants determined in each case for the new fractions. Refractionation was carried out in a systematic fashion. Since pressure was carefully controlled throughout all the distillations, distillation temperature served very satisfactorily as a guide to indicate the appropriate time for adding, during the course of distillation, the successive fractions from the previous series.

As the total number of fractions involved is very large, only such fractions are tabulated (Tables I, II and III) as show significant changes in properties—maxima or minima in density, refractive index and rotation. The intermediate fractions which exhibited properties in between those listed are omitted.

The first fractionation gave fractions 1 to 24 and these in turn were refractionated giving the series 1A to 32A.

Since the properties of the first series of 24 fractions are reflected in those of the refractionation (Series 1A–32A) with the corresponding maxima and minima more marked, no space is taken to tabulate the data on the first series.

Table I gives the data on the significant fractions of the A series.

TABLE I

DATA ON SIGNIFICANT FRACTIONS OF THE A SERIES OBTAINED BY REFRACTIONATION OF THE FIRST SERIES (1 TO 24)

Fraction	Dist. temp., °C.	Mm. press.	Wt., g.	n^{20}_{D}	Density 15.5°	α_D Angular rotation	Dominant constituent	
1A	53–55	20	2	1.4619	0.8522	+19.7	or-Pinene	
2A	55–62	20	4	1.4633	.8366	+15.2		
5A	65–65.2	20	31	1.4656	.7977	+ 2.6	Myrcene	
6A	65.2	20	20	1.4657	7979	+ 2.6	Myrcene	
12A	66.2–67.2	20	15	1.4672	.8130	+ 5.8	Phellandrene	+ Cineol Citral
18A	70.5–70.7	20	16	1.4665	.8702	–25.9	Dipentene and Limonene	
23A	53.4–66	7	8	1.4738	.8421	– 8.3		
25A	74.4–76	7	8	1.4625	.8728	–10.6		
29A	88–91.4	7	7	1.4785	.9219	+ 4.3	Analcohol	
32A	96 up	1	16	1.4864	.9098	0		

A graph showing the rotation data of the series is given in Fig. 1.

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(8) Marshall and Sutherland, Ind. *Eng. Chem.*, 19, 735 (1927).

Of this series, 4A to 23A (inclusive) were again refractionated, giving the new series of fractions designated 4B to 25B. Fractions 1A to 3A (inclusive) were too small to be included in this refractionation. This was also the case with fractions 24A to 32A (inclusive) after being deprived of citral as described later. Data on the significant fractions of this series are given in Table II.

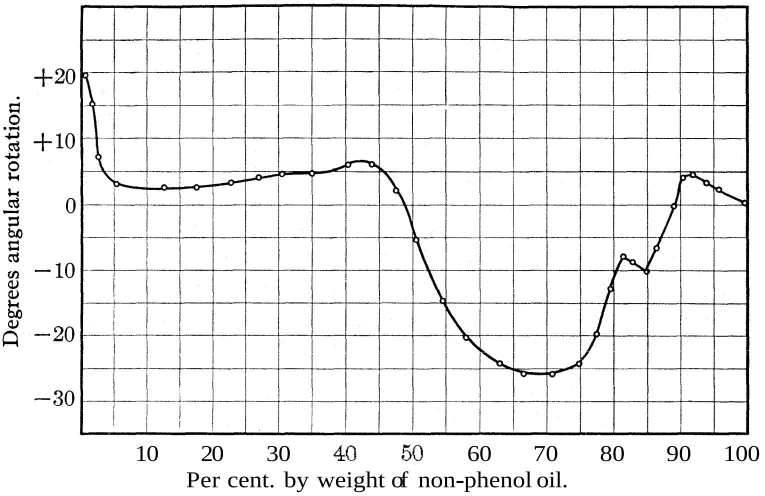

Fig. 1.—Observed rotation of non-phenol portion of bay oil.

TABLE II

DATA ON SIGNIFICANT FRACTIONS OF THE B SERIES OBTAINED BY REFRACTIONATION OF 4A–23A

Fraction	Dist. temp., °C.	Press., mm.	Wt., g.	n^{20}_{D}	Density 15.5°	α_D Angular rotation	Dominant constituent	
5B	65–65.2	20	18	1.4649	0.7973	+ 2.2	Myrcene	
6B	65.2–65.4	20	14	1.4650	.7966	+ 2.5	Myrcene	
12B	66–66.2	20	12	1.4674	.8079	+ 7.6	Myrcene and Phellandrene	
13B	66.2–67.8	20	15	1.4673	.8224	+ 6.7	Phellandrene	+ Cineol
19B	70.6	20	20	1.4666	.8684	−26.4	Dipentene and Limonene	
20B	70.6–70.7	20	15	1.4668	.8663	−27.2	Dipentene and Limonene	
25B	51	1.5	10	1.4727	.8397	− 8.7		

Cineol was removed from fractions 12B to 24B as described later, and the cineol free fractions were refractionated, giving the series 1C to 9C.

Data on the significant fractions of this series are given in Table III.

In view of the prolonged period over which fractionation had to be made, some polymerization (myrcene and phellandrene both tend to polymerize) was unavoidable even at the comparatively low temperatures involved. The polymer dimyrcene was indicated toward the end of the distillation.

Removal of Aldehyde.—Fractions 24A to 32A gave a positive qualitative reaction for aldehyde when tested in an alcoholic solution with a few drops of fuchsine reagent An alcohol blank was used for control. These aldehyde-containing fractions were ex-

TABLE III

SIGNIFICANT FRACTIONS OF THE C SERIES OBTAINED BY REFRACTIONATION OF 12B–24B AFTER REMOVAL OF CINEOL

Fraction	Dist temp., °C.	Press., mm	Wt. in g	n^{20}_{D}	Density 15 5°	α_D Angular rotation	Dominant constituent
1C	65 5–67	20	9	1.4682	0.8192	− 2.8"	
7C	70.2	20					
	to 49	7	10	1.4704	.8568	−31.7°	Dipentene and Limonene
8C	49–51.2	7	10	1 4727	.8519	−35 8°	Dipentene and Limonene
9C	Residue in col.	1	7	1 4765	.8429	-33 5°	Dipentene and Limonene

tracted several times with bisulfite solution, washed free from the reagent and used for subsequent examination. The aldehyde was liberated from the bisulfite compound and identified as described under citral.

The total residual oil left from 24A to 32A after removal of aldehyde was too small to permit refractionation.

Removal of **Cineol.**—Fractions 12B to 24B, which had a strong eucalyptol-like odor, were extracted several times with 50% resorcinol as described later under cineol. The residual cineol-free oil was thoroughly washed with water until free from resorcinol as shown by ferric chloride tests of the washings, dried and refractionated, giving the series of fractions 1C to 9C of Table III as previously mentioned.

Examination of the Fractions

α-Pinene (Fractions 1A and 2A).—The nitrosyl chloride. In view of the very small quantity available for this examination, details of the procedure used for the preparation of the nitrosyl chloride with but 1 cc. of oil are here given as follows (adapted from the modified Lynn procedure).[9] A mixture of 1 cc. of the oil (fraction 1A), 1 cc. of 95% alcohol and 1 cc. of ethyl nitrite in a test-tube was well cooled in an ice-bath and to it was added, drop by drop, with vigorous stirring, 0.85 cc. of 8 N alcoholic hydrochloric acid. After standing for about one hour in the ice-bath with occasional shaking, the precipitate was filtered off by suction, using a micro filtering arrangement, and washed. The dry precipitate was purified in the usual manner by dissolving it in a minimum quantity of chloroform and adding methanol, crystallization taking place almost immediately; m. p. 104–105°.

This is the nitrosyl chloride of the inactive form, which comes out first.

Myrcene (Tetrabromide of the Dihydromyrcene).—Dihydromyrcene was prepared from fraction 4B by reduction with sodium and alcohol and then converted to the tetrabromide, in general as described by Enklaar.[10]

Recovery of the tetrabromide from the oily by-products by the Enklaar method was virtually impossible. The following procedure yielded an excellent crystallization. (a) The oily layer obtained by pouring the brominated reaction mixture into water was drawn off in a separatory funnel (without preliminary dissolving in ether), and washed several times with sodium carbonate solution, then with water. (b) The acid aqueous layer was extracted with ether The ethereal layer was washed as above, the bulk of the ether evaporated in vacuum, and the residual oil was combined with the original oil from (a). The total oil was then shaken several times with cold 95% alcohol, which is a good solvent for the oily by-products and with which the tetrabromide formed an immiscible layer, The tetrabromide thus purified, on dissolving in warm absolute alcohol and allowing to stand, gave excellent crystals. The product, after one recrystallization from absolute alcohol, melted sharply at 88°.

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(9) Lynn, THIS JOURNAL, 41, 361 (1919).

(10) Enklaar, Rec. *trav. chim.*, 26, 164 (1907).

Purification of Myrcene

Previous reports on myrcene by Power and Kleber[3] and Enklaar.[10] show that these authors found this compound optically inactive or nearly so, density at 15°, 0.8013 and refractive index 1.4700.

Attempts were made to prepare a pure optically-inactive myrcene by fractional crystallization of the myrcene fractions, liquid air being used as a refrigerant, since repeated fractional distillation did not yield the hydrocarbon entirely free from optical activity. The "freeze" produced, however, was very sirupy, too thick to permit filtration. It is presumed that the persistent optical activity in myrcene fractions is due to α-phellandrene.

The inactive myrcene obtained by Power and Kleber and Enklaar may, perhaps, be accounted for by the presence of nearly balanced proportions of phellandrene (positive rotation) and limonene (negative rotation) The minimum density (see Table II) of the myrcene obtained in this investigation would seem, if anything, to indicate a higher purity than that previously reported since both compounds, α-pinene immediately preceding and α-phellandrene immediately following myrcene in the fractionation, have considerably higher densities.

The properties of this compound are accordingly as shown in Table II, fraction 6B: $d^{15.5}_{4}$ 0.7966; n^{20}_{D} 1.4650, b. p. 65–66° (20 mm.) and 166–167° (760 mm.).

Phellandrene.—The nitrosite was prepared from fraction 12B by treating a well-cooled mixture of 5 cc. of the oil in about 15 cc. of petroleum ether and 5 cc of a saturated solution of sodium nitrite with glacial acetic acid, drop by drop, until about 5 cc. of the acid was added—shaking continuously. A pasty mass was obtained, which after the supernatant liquid was poured off was washed by kneading several times in cool water, the wash water being poured off. This mass was then taken up in methanol, the yellow precipitate so obtained filtered, washed several times with small quantities of cold methanol and then recrystallized from chloroform and ether; m. p. 104–105°.

Several attempts were made to prepare a nitrosyl chloride from these fractions, but none was obtained, showing apparently that α- and not β-phellandrene is here involved.[11]

Cineol (Fractions 12B to 24B).—(a) Cineol hydrobromide was prepared by allowing gaseous hydrobromic acid to flow over (rather than through) a petroleum ether solution of the oil well-cooled in an ice-bath while shaking gently to facilitate absorption of the gas. The crystalline mass was then filtered by successive washing with petroleum ether and dried; m. p. 56–57°.

(b) Cineol–Resorcinol. Addition Compound.—The oil when shaken with 50% resorcinol solution became practically a solid crystalline mass. The crystals after filtration and washing with water and then with petroleum ether and drying, had a melting point 79–80°. The cineol, regenerated in the usual manner, possessed the characteristic odor of this compound.

Citral (Fractions 24A to 32A).—The oil was treated in the usual way with cold concentrated sodium bisulfite solution. Only the fresh reagent prepared by passing sulfur dioxide through a saturated solution of sodium carbonate was found effective. Some of the fractions rich in citral, when treated with the bisulfite, became a solid crystalline mass. The citral was regenerated from the well-cooled bisulfite with alkali in the usual manner It possessed the characteristic odor and gave with β-naphthylamine and pyruvic acid the characteristic yellowish β-naphthylcinchoninic acid which on recrystallization from alcohol melted at 195°.

Dipentene and **Limonene** (Fractions 5C to 9C). (a) Tetrabromide.—No difficulty was encountered in preparing the tetrabromide by the Godlewski procedure.[12] The product was subjected to fractional crystallization in an effort to prepare the limonene

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[11] Francesconi and Sunagiotto, *Atti accad. Lincei*, [V] 20, 1, 325 (1911).

[12] Godlewski, *Chem.-Ztg.*, 22, 827 (1898).

tetrabromide, but this was not accomplished on account of the predominating proportions of dipentene; m. p tetrabromide 123–124°.

(b) Nitrosyl Chloride.—A nitrosyl chloride was prepared by the method described for α-pinene with the exception that glacial acetic acid was also added in addition to the alcoholic hydrogen chloride. The somewhat pasty mass produced at first became crystalline on addition of the acetic acid; melting point of limonene nitrosyl chloride 103–104°.

Nitrosite.—In view of the belief that the negative rotation of bay oil was due to α-phellandrene,[3] an effort was made to prepare a nitrosite from fraction 9C but without success. Phellandrene was identified only in positive fractions immediately following the myrcene.

An Alcohol (Unidentified).—Fractions 28A to 32A, after removal of citral, possessed a very pleasant geraniol- or nerol-like odor. These fractions, after removal of citral, were very small (a few grams total). An approximate estimation of the alcohol content of 32A, on about 0.4 g. showed this fraction to contain about 23% alcohol calculated as $C_{10}H_{18}O$ **A** separation of the alcohol from the indifferent oil on the combined fractions 28A to 32A was made by way of the boric acid esters. the Schmidt procedure,[13] being used. The yield of ultimate "alcohol" was very small.

No crystalline phenylurethan or diphenylurethan could be isolated. The oil, however, gave a pronounced violet-red color reaction with alcoholic hydrobromic acid and with concentrated sulfuric acid similar to that obtained by Erdmann and Huth[14] for rhodinol and linalool.

Methylchavicol **and** Methyleugenol.—Anise-scented fractions, reported by previous investigators, were not encountered in any of the fractionations.

A determination of mcthoxyl on 24A, 28A and 32A by the modified Vieböck and Schwappach method,[15] 30–50 mg. being used for a determination, showed a methoxyl content as follows: 24A—0.41%; 28A—1.08%; 32A—4.71%. Since these fractions totaled but a few grams, the maximum content of methyl ethers in the original bay oil, if present at all, would seem to be negligible. The quantities in the fractions were too small to permit identification.

Oil from the anise-scented variety of *Pimenta acris* has been shown by Warneford[16] to contain about 15% estragol (methylchavicol).

In the usual harvesting of bay leaves by the natives, an admixture of leaves from the anise-scented and limoncilla varieties is almost unavoidable unless collected under the careful supervision of an experienced botanist. It is barely possible that the bay leaves used by Power and KIeber[3] contained appreciable quantities of the anise-scented variety, and this may account for their findings with regard to the methyl ethers.

Esters.—Fractions 28A to 32A possessed a rather sweet odor. It was thought that this might, in part, be ascribable to an ester. Saponification of small samples with alcoholic potash in the usual manner indicated no more than a trace to be present.

Acknowledgment.—The authors are pleased to acknowledge their indebtedness to Dr. W. W. Skinner for his many valuable suggestions during the progress of this work.

Summary

With the aid of an improved vacuum fractionating assembly, here described, oil of bay has been subjected to a more critical examination than heretofore.

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(13) Schmidt, *Chem.-Ztg.*, **52**, 898 (1928).

(14) Erdmann and Huth, *J. prakt. Chem.*, 56, 4 (1897).

(15) Clark, *J. A. O. A. C.*, **15**, 136 (1932).

(16) Warneford, *Trop. Agri. (Trinidad)*, 4, 128 (1927); *C. A.*, **22**, 2238 (1928).

The present investigation, relating to the non-phenol portion of the oil, shows that previous conclusions regarding its composition are erroneous in several particulars.

The following composition is indicated: myrcene, cineol and dipentene, with limonene are the predominating constituents; citral, a small amount of α-phellandrene and, contrary to previous reports, a small amount of α-pinene and but little, if any, methylchavicol and methyleugenol are present. A small amount of a geraniol-like alcohol was also found, but its identity was not determined.

WASHINGTON, D. C. RECEIVED AUGUST 19, 1932
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[CONTRIBUTION FROM INDUSTRIAL-FARM PRODUCTS DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Crystallizable Chavicol and Eugenol from the Oil of Bay[1]

BY S. PALKIN AND P. A. WELLS

As indicated in another paper[2] the major portion of the oil of bay (obtained by steam distillation of the leaves of *Pimenta acris*) consists of phenols.

As early as 1877 Markoe[3] had already observed the presence of eugenol in the "heavy oil of bay."[4] This term is applied to the oil coming over in the latter part of the distillation, which is rich in phenols.

Mittmann,[5] who made an examination of the whole oil, concluded that eugenol was the only phenol present, but Power and Kleber,[6] in a more comprehensive investigation of the oil, established the presence of another phenol, namely, chavicol. These authors were unable to separate the phenols as such but proved the presence of chavicol and eugenol by converting the total phenol portion to the methyl ethers and fractionating these.

So far as we are aware, however, chavicol as such has never been isolated from the oil of bay nor has the pure eugenol been prepared from this source.

In a recent investigation of the composition of bay oil, fractionation of the phenol portion with the aid of pressure-controlled plate columns made possible a very effective separation of the two phenol constituents. The chavicol fractions so obtained in one fractionation solidified to a beautiful crystalline mass on moderate cooling.

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(1) Presented before the Division of Medicinal Chemistry, Denver Meeting of the American Chemical Society, September 22–26, 1932.

(2) Palkin and Wells, THIS JOURNAL, **55**, 1549 (1933).

(3) Markoe, *Proc. Am. Pharm. Assoc.*, p. 438 (1877).

(4) This term is applied to the oil coming over in the latter part of the distillation, which is rich in phenols.

(5) Mittmann, *Ber.*, 27, 352 (1894).

(6) Power and Kleber, *Pharm. Rundschau*, 18, 60 (1895).

Eykman[7] cooled chavicol which he purified from betel oil to −25° without effecting crystallization.

By repeated fractional distillation and fractional crystallization, both chavicol and eugenol were prepared in a high state of purity and their physical properties determined.

Experimental Work

Preparation of the Phenol Portion.—The general procedure for the separation of the nor, phenol portion, of bay oil from the phenols is described in the other publication.2 To recover the phenols, the solution of alkali phenolate so obtained was well cooled, and the phenols were liberated with 10% sulfuric acid (a slight excess). The bulk of the oil was separated by centrifuging, and the oil dissolved in the water was obtained by extraction with ether. Both the bulk of phenol oil and the ethereal extract were thoroughly washed with water until free from acid. The ether was distilled off in vacuum, the phenol residue from this added to the main portion of phenol, and the moisture removed by distillation in vacuum. The proportion of eugenol in the total phenol, obtained by way of a methoxyl determination, was found to be 89.3%, or the chavicol content, by difference, 10.7%.

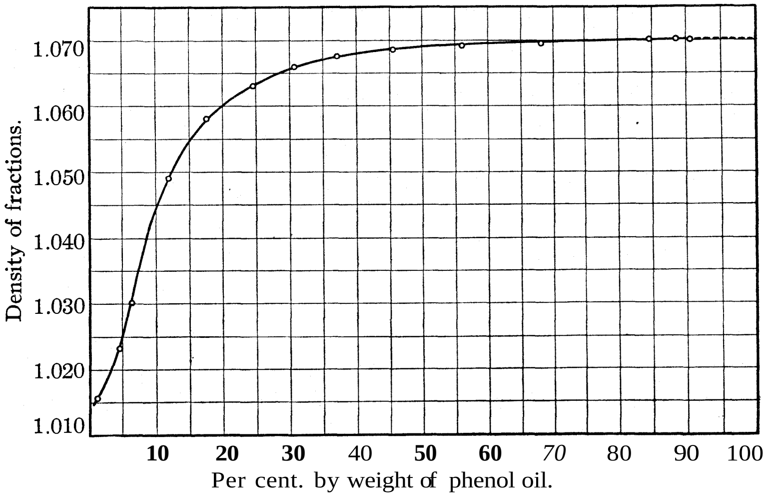

Fig. 1.—Density of phenol portion of bay oil.

Fractionations.—The phenol oil (900 g.) was fractionated in a large 32-plate column at 7 mm. up to the last 100 g., fractionation of the latter being completed in the small 20-plate column. The density and refractive index were taken for each fraction. The series of fractions so obtained distilled between 105.4 and 114°. The density (Fig. 1) and refractive index gave no indication of other phenols.

The plate column assemblies used in this investigation are described in another paper in THIS JOURNAL.[2]

Preparation of Pure **Chavicol.**—For further purification of chavicol, the first fractions were systematically refractionated. Of eleven fractions so obtained the first nine were again refractionated.

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(7) Eykman, *Ber.*, 22, 2739 (1889).

Fractional Crystallization.—The fractions distilling between 103.2 and 103.6° at 7 mm. (density ranged from 1.0190 to 1.0200 and refractive index from 1.5426 to 1.5436) were combined and subjected to five crystallizations. The solid portion of the fifth was again fractionally distilled and examined for density, refractive index, quantity of methoxyl, etc.

The chavicol thus prepared had the following properties: m. p. 16°; b. p. 235–236°; n^{20}_{D} 1.5448; $d^{15.5}_{4}$ 1.0203; methoxyl (0.050 and 0.048% or 0.26% calculated as eugenol). On this basis the chavicol is over 99.7% pure.

Determination of methoxyl was found to be a convenient guide in following the purity (pertaining to freedom from eugenol) of the chavicol.

The technique involved in the crystallization was somewhat as follows. A jacketed Gooch filtration arrangement was used, the upper half of an ether can serving as a jacket, and a crucible with a coarse sintered glass bottom (No. 1 or 2) as the filtering device. A few pieces of ice in the jacket provided sufficient insulation. The sample to be recrystallized was cooled in an ice and salt bath to the consistency of a "slush" by stirring vigorously while in the cooling bath. This was then transferred to the filter device and moderate suction applied as soon as the filter plate was fully covered. Care must be taken in this operation to keep the crystalline portion pressed down to a compact mass in the crucible, as otherwise channeling occurs, warm air is pulled through, and it is not possible to suck the mass dry.

Chavicol 3,5-dinitrobenzoyl ester was prepared without any difficulty by the method of Phillips and Keenan,[8] m. p. 103.5–104.5°.

Purification of the Eugenol.—Of the first fractionation of the original mixture of phenols, the last five fractions distilling between 113.8–114° at 7 mm. were practically all eugenol, the properties of the fractions corresponding well with those reported for eugenol from other sources. The density ranged from 1.0690 to 1.0701, and the refractive index from 1.5403 to 1.5405.

These were combined and fractionally distilled, then fractionally crystallized, more or less as described for chavicol, and again distilled in vacuum. Solid carbon dioxide was used as the refrigerant instead of ice. Properties of purified eugenol so prepared are as follows: m. p. −7.5°; b. p. 254°; n^{20}_{D} 1.5405; $d^{15.5}_{4}$ 1.0701; methoxyl, 18.79%; calcd., 18.92%. The 3,5-dinitrobenzoyl ester prepared as described above had a melting point of 130–131°.

Acknowledgment.—The authors are pleased to acknowledge their indebtedness to Dr. W. W. Skinner for his many valuable suggestions during the progress of this work.

Summary

By means of repeated fractional distillation and fractional crystallization of the phenol portion of bay oil, chavicol and eugenol of high purity were obtained, which crystallized at +16 and −7.5°, respectively.

The method of preparation used and data on the properties of the purified phenols so obtained are given.

WASHINGTON, D. C.

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[8] Phillips and Keenan, THIS JOURNAL, 53, 1924 (1931).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Yields of Some Aliphatic Tertiary Grignard Reagents and the Limits of their Usefulness as Synthetic Reagents

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Researches on rearrangements being conducted in this Laboratory required a variety of compounds containing the grouping $R_3CC(OH)R'_2$.[2] in which R represents various alkyl groups and R' represents alkyl or hydrogen. The preparation of these substances by means of the Grignard reaction presented two uncertainties, (1) the decreased yield of Grignard reagents of higher molecular weight especially from tertiary halides which lose halogen acid readily and (2) the limited yields of the desired products obtainable from highly branched Grignard reagents.[3] To obtain information on these points was the purpose of this research.

The literature contains little information on tertiary aliphatic Grignard reagents higher than tertiary amyl. Preliminary studies showed that tertiary chlorides give higher yields of Grignard reagents than the corresponding bromides and iodides. In the present work the following chlorides have been investigated: tertiary butyl, tertiary amyl, dimethyl-*n*-butylcarbinyl, dimethyl-n-amylcarbinyl, methyldiethylcarbinyl, methylethyl-n-propylcarbinyl, methylethyl-n-butylcarbinyl, and triethylcarbinyl. Yields of Grignard reagents from these chlorides varied from 60% for dimethyl-n-amyl- and triethylcarbinyl chlorides to 83% for tertiary butyl chloride. All yields were determined by titration of aliquot samples of the clear Grignard solution according to Gilman.[4]

More magnesium chloride was formed during the preparation of the Grignard reagent from the higher tertiary halides. The large amount of olefin which was usually isolated from the reaction mixtures in such cases indicated the withdrawal of hydrogen chloride from the chloride by the magnesium.

The results indicate that the higher tertiary Grignard reagents are not suitable for syntheses which involve the addition of the Grignard reagent to the carbonyl group of a ketone or ester. They can be used to some extent, however, when an active halogen is present, as in the case of ethyl chlorocarbonate and (to a certain extent) acetyl chloride. The reaction with carbon dioxide and with formaldehyde in most cases proceeds normally, although the yields of the desired acid or primary alcohol are not as high as in the case of the lower chlorides.

The reaction between tertiary-butylmagnesium chloride and ethyl

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(2) (a) Whitmore, THIS JOURNAL, 54, 3274 (1932); (b) Whitmore and Woodburn, *ibid.*, 55, 361 (1933); (c) Whitmore and Williams, *ibid.*, 55, 406 (1933).

(3) Conant and Blatt, *ibid.*, 51, 1227 (1929).

(4) Gilman, *ibid.*, 45, 150 (1923).

carbonate was investigated. The reaction proceeds only to the first step, *i. e.*, to the ethyl ester of trimethylacetic acid. This is to be expected since Conant and Blatt[5] have reported that there is little or no reaction between ethyl trimethylacetate and tertiary-butylmagnesium chloride. Tertiary-amylmagnesium chloride did not react at all with ethyl carbonate in ethyl ether. With higher boiling solvents (benzene and toluene) a very small amount of the ethyl ester of dimethylethylacetic acid was isolated.

The reaction with ethyl chlorocarbonate, however, is more general. Both tertiary-butyl- and tertiary-amylmagnesium chlorides yield with this reagent the ethyl ester of the trisubstituted acetic acid. This reagent also reacts with the higher tertiary Grignard reagents. Dimethyl-*n*-butylcarbinylmagnesium chloride yielded the ethyl ester of dimethyl-*n*-butylacetic acid.

The reaction between acetyl chloride and the tertiary Grignard reagents was investigated. In each case the ether solution of Grignard reagent was added to an excess of acetyl chloride in ether. From tertiary-butylmagnesium chloride and acetyl chloride was obtained pinacolone in yields large enough to compete with the older process for making this ketone. Tertiary-amylmagnesium chloride and acetyl chloride yielded methyl tertiary-amyl ketone but in lower yield. With methyldiethylcarbinylmagnesium chloride and dimethyl-n-butylcarbinylmagnesium chloride the yields of the corresponding ketones were still lower.

Four of the higher tertiary Grignard reagents were treated with formaldehyde to give homologs of neopentyl alcohol. The study of these alcohols, especially their dehydration with rearrangement, is being continued.

Experimental

Description of Distillation Apparatus.—The fractionating columns used in the various distillations will be referred to by number:[5] Column I, total reflux type, asbestos insulated, packed with 5 × 5 mm. glass rings, 68 X 1.8 cm.; Column II, same but 35 X 2.1 cm.; Column IV, total reflux type, electrically heated jacket, indented, 63 X 1.1 cm. The dimensions, in Columns I and II, are those of the packed sections, and in Column IV, of the indented section.

Preparation of the Tertiary Halides.—The tertiary carbinols (with the exception of the butyl and amyl alcohols[6]) were prepared as indicated in Table I.

The chlorides of these carbinols were prepared by saturating the carbinols with dry hydrogen chloride at 10–15°. The upper (halide) layer was washed once with a cold saturated aqueous solution of potassium carbonate, and dried over anhydrous potassium carbonate for at least twenty-four hours. The halide was then distilled under reduced pressure in the presence of 2 g. of anhydrous potassium carbonate to combine with any liberated acid. The tertiary carbinols and halides were fractionated through Column II.

Preparation of the Tertiary Grignard Reagents.—The main difficulty encountered in preparing the higher tertiary Grignard reagents was that of inducing the reaction to start. The usual expedients were followed.

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(5) *Cf.* Whitmore and Lux, THIS JOURNAL, 64, 3451 (1932).

(6) These were supplied by the Hydrocarbon Products Company of New York and the Sharples Solvents Corp. of Philadelphia, respectively

TABLE I

PREPARATION AND PROPERTIES OF THE TERTIARY CARBINOLS AND CHLORIDES

		Preparation					Tertiary chloride		
	Tertiary carbinol	Carbonyl compd.	Grignard	Yield,[a] %	B. p. range	n^{20}_D	B. p. range, °C.	Yield,[e] %	n^{20}_D
1	$CH_3(C_2H_5)_2COH$	$CH_3COC_2H_5$	C_2H_5MgBr		[d]		68–69/160[d]	59[f]	1.4208
2	$CH_3(C_2H_5)(n\text{-}C_3H_7)COH$	$CH_3COC_2H_5$	C_3H_7MgBr	65.6 82.3[g]	56/20 to 52/16	1.4231	62–63/52	90	1.4250
3	$CH_3(C_2H_5)(n\text{-}C_4H_9)COH$	$CH_3COC_2H_5$	C_4H_9MgBr	70.6	64–65/16[b]	1.4283	64–65/27[b]	92	1.4314
4	$(CH_3)_2(n\text{-}C_4H_9)COH$	CH_3COCH_3	C_4H_9MgBr	64.6 70.5[g]	65/35 to 63/29[b]	1.4179[b]	69–72/90[b]	75	1.4202[b]
5	$(CH_3)_2(n\text{-}C_5H_{11})COH$	CH_3COCH_3	$C_5H_{11}MgBr$	63	65–66/15[e]	1.4235	49.5–51/15'	81	1.4250
6	$(C_2H_5)_3COH$	$(C_2H_5)_2CO$	C_2H_5MgBr	74	72–73/52	1.4294	64–65/52	88	1.4329

[a] These are yields of products of the boiling range indicated. They are calculated on the halide used [b] *Cf.* Ref. 2(b). [c] *Cf.* Ref. 2(c). [d] Favorski and Zalessky–Kibardine give for the carbinol b. p. 121" (755 mm.) and for the chloride b. p 111° (761 mm.) and 85° (280 mm.), *Bull. soc. chim.*, [4] 37, 1230 (1925). [e] Yields of products of indicated boiling range, calculated on the carbinol used. [f] Calculated on the ethyl bromide used in making the carbinol. [g] Calculated on the Grignard reagent.

The procedure in preparing the Grignard reagents is, with one or two minor exceptions, that found bv A. R. Lux of this Laboratory to give good yields of tertiary-butylmagnesium chloride.[7] As has been noted by Gilman and his co-workers,[8] it is essential that the halide–ether solution be added to the reaction mixture slowly. Any considerable deviation from the procedure described, such as varying the amount of ether used, etc., results in an appreciably lower yield of Grignard reagent. Vigorous and thorough agitation of the reaction mixture is essential. It is not necessary to use an excess of magnesium.

A typical procedure as used is given herewith. The procedure described is for a four-mole run, the same proportionate amounts of materials being used for smaller or larger runs.

In a 3-liter 3-necked round-bottomed flask fitted with an efficient stirrer, reflux condenser and dropping funnel are placed first a few small crystals of iodine and then 98 g. (4 moles) of fresh magnesium turnings. The bottom of the flask is heated with a small flame until the iodine commences to vaporize and is then allowed to cool while the halide is being weighed out. Thirty cc. of a mixture of four moles of the tertiary halide and 500 cc. of dry diethyl ether is added directly to the dry magnesium. After reaction has started and progressed for a few minutes, 200 cc. of dry ether is added directly to the reaction mixture. Four hundred and seventy-five cc. of the above halide-ether solution is placed in the dropping funnel and added with stirring at a rate not faster than one drop every second. It is advisable to add the halide–ether even more slowly

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[7] For example, a nine-mole preparation of trimethylacetic acid resulted in a 75% yield of pure acid, based on the tertiary-butyl chloride used.

[8] Gilman and co-workers, THIS JOURNAL, 60, 425 (1928).

in the case of the higher tertiary halides. The remainder of the halide–ether solution is diluted with 300 cc. of dry ether and added at the same rate with stirring after the first portion is added. The mixture is allowed to reflux during the halide-ether addition, no external cooling being applied. It is unnecessary to heat the mixture after the halide–ether solution has been added Stirring is continued for an hour. Before titrating for yield the flask containing the Grignard reagent solution is stoppered and left overnight to allow suspended material to settle completely.

In several cases (noted in Table II) reaction did not start upon addition of the first 30 or 40 cc. of halide–ether solution. When this was the case, the addition of a few drops of a more reactive halide, such as ethyl- or n-butyl bromide, usually started the reaction.

TABLE II

PREPARATION AND YIELDS OF GRIGNARD REAGENTS OF TERTIARY CHLORIDES

Halide	Moles	Halide–ether addition, hrs	Yield	Notes
$(CH_3)_3CCl$	3	Note *d*	80	*a*
$(CH_3)_2(C_2H_5)CCl$	3	Note *d*	73 6	b
$(CH_3)_2(n\text{-}C_4H_9)CCl$	1.5	7.0	74.4	*a*
	1.5	9.5	79.0	*a*
$(CH_3)_2(n\text{-}C_5H_{11})CCl$	1.5	14	59.9	*g*
$CH_3(C_2H_5)_2CCl$	1.5	Note *d*	70.4[e]	b
$CH_3(C_2H_5)(n\text{-}C_3H_7)CCl$	1.5	7.7	67.4	*b*
	3.3	24	75.8	b
	4.5	52	77.7	c
	5.0	90	75.8	a
$CH_3(C_2H_5)(n\text{-}C_4H_9)CCl$	4	77	70.0	*c*
$(C_2H_5)_3CCl$	1.4	6.0	58.3	*f*

[a] Reactions started almost immediately. [b] Reactions started within fifteen minutes. [c] Necessary to add 1 cc. of n-butyl bromide and additional iodine to start the reaction. [d] "Not over 1 drop per sec." [e] In this Laboratory, H. S. Rothrock and K. C. Laughlin have obtained yields of the Grignard reagent of 65 and 72%, respectively. Faworski and Zalessky–Kibardine obtained a 34% yield. [f] Necessary to add 1 cc. of ethyl bromide to start reaction. [g] Necessary to add a few drops of methyl iodide and more iodine to start the reaction.

In preparing those Grignard reagents in which the olefin which is formed is not a gas it is advisable to connect the outlet of the apparatus to a sulfuric acid trap to exclude atmospheric moisture.

Ethyl Carbonate and Tertiary-butylmagnesium Chloride.—To 3.8 moles of tertiary-butylmagnesium chloride in 1500 *cc.* of ether was added, with stirring, 450 g. (3.8 moles) of ethyl carbonate (b. p. 125° (734 mm.)). The reaction was mild. The mixture was refluxed on the water-bath during the addition. As reaction progressed a pasty solid separated and the mixture became quite viscous, making stirring difficult. Stirring was continued for two hours after the addition was complete. The mixture was decomposed on ice and enough dilute sulfuric acid was added to dissolve the precipitate. The layers were separated and the aqueous layer extracted three times with 100-cc. of ether. The ether solutions were dried overnight with 75 g. of anhydrous potassium carbonate.

The ether was distilled off through a small packed partial condensation column and the residue was distilled through Column I with a high reflux ratio to give the following fractions with the weights and boiling points (740 mm.) indicated: (1) 16 5, 77–80°; (2) 10.0, 80–83°; (3) 75, 83–117°; (4) 280.0, 117–118.5°, n_D^{20} 1.3888: (5) 125.0, 118.5–126°.

Fraction (4) represented a 56% yield of ethyl trimethylacetate based on the Grignard reagent used Its saponification products were identified by means of solid derivatives.

Ethyl Carbonate Tertiary-amylmagnesium Chloride.—A reaction carried out in the same way as with the tertiary-butylmagnesium chloride yielded only unchanged ethyl carbonate.

In another experiment, after the Grignard reagent had been prepared, benzene was added and the ether was distilled off through a small column. The calculated amount of ethyl carbonate was added The reaction mixture was maintained at 60–70° for several hours. Upon working up in the usual way only a trace of the ethyl ester of dimethylethylacetic acid was obtained. Another reaction carried out in the same way except that toluene was used in place of benzene also gave only a trace of the ester. A total of 20 g. of the ester was obtained in the last two reactions from a total of 1.66 moles of tertiary-amylmagnesium chloride. The ester boiled at 140–141° It was identified by saponification.

Ethyl Chlorocarbonate and Tertiary-butylmagnesium Chloride.—To 2 2 moles of tertiary-butylmagnesium chloride in 900 cc. of ether solution was added 244.2 g. (2.25 moles) of ethyl chlorocarbonate, b. p. 91–92.5° (741 mm.), in 500 cc. of ether at a rate of 2 to 3 drops per sec., with stirring. The mixture was allowed to reflux from the heat of reaction. A gray precipitate separated rapidly, soon making stirring difficult. At the end of the reaction the mixture was almost solid. This did not break up when 200 cc of ether was added and the mixture stirred vigorously. The mixture stood overnight and was then decomposed on ice. Most of the solid dissolved. Ammonium chloride was added to dissolve the small amount of gelatinous precipitate. The mixture was worked up in the usual way except that the crude product was refluxed and stirred with sodium bicarbonate solution to remove unreacted chlorocarbonate. The product was then dried over 15 g. of anhydrous sodium sulfate and fractionated at 737 mm. through Column I to give the following fractions: (1) 9.5 g.. 112–115°; (2) 9.0 g., 115–116"; (3) 18.0 g. 116–117"; (4) 135.0 g., 117°, n^{20}_{D} 1.3890; (5) 15.5 g. of residue. Fractions 2–4 were identified as ethyl trimethylacetate, yield 56% based on the Grignard reagent. This yield could undoubtedly be increased by using a larger volume of ether so as to permit more efficient stirring.

Ethyl Chlorocarbonate and Tertiary-amylmagnesium Chloride.—To 1.97 moles of tertiary-amylmagnesium chloride in a total volume of 1020 cc. was added with stirring and refluxing (water-bath), at a rate of 1 to 2 drops per second, 212 grams (1.97 moles) of ethyl chlorocarbonate. After the addition, the reaction mixture was refluxed and stirred for five hours. A gray precipitate gradually separated. The water-bath was removed and the mixture stirred overnight. In the morning the mixture was almost solid. It was refluxed with stirring for four hours longer and then treated as usual. The product was fractionated at 735 mm through Column I, giving (1) 51 2 g., 128–140°; (2) 116.9 g., 140–141°; and a residue of 36.9 g. Fraction 2 was identified as ethyl dimethylethylacetate, yield 46% based on the Grignard reagent.

Ethyl Chlorocarbonate and Dimethyl-*n*-butylcarbinylmagnesium Chloride.—Six hundred cc. of a filtered ether solution of 0.99 mole of dimethyl-*n*-butylcarbinylmagnesium chloride was added during two hours to 116 g. (1.07 mol) of ethyl chlorocarbonate in 200 cc. of dry ether. The reaction was vigorous and accompanied by the formation of a white precipitate. The mixture was allowed to reflux. The mixture stood overnight and was then worked up in the usual way. The product was fractionated through Column II at 735 mm. for the first three fractions and at 16 mm. for the last three to give: (1) 17.2 g., 86–90'; (2) 27.9 g., 90–94°; (3) 3.9 g., 94–106°; (4) 16.6 g., 106" (735 mm.) to 66.5' (16 mm.); (5) 47.1 g., 66.5–70.0° (16 mm.), n^{20}_{D} 1.4148; (6) 7.7 g., 70–105.5' (mainly 103–105.5° (16 mm.)), n^{20}_{D} 1.4225. Fraction 5 was identified as ethyl dimethyl-n-butylacetate. This was converted to dimethyl-n-butylacetamide. m. p. and mixed m. p. 92.8–93.8'. Fractions 1 and 2 decolorized bromine solution.

Acetyl Chloride and Tertiary-butylmagnesium Chloride.[9]—Nine hundred cc. of a filtered solution of 2.26 moles of tertiary-butylmagnesium chloride was added to 236 g. (3 moles) of redistilled acetyl chloride in 600 cc. of dry ether during six hours with stirring. The reaction was vigorous. A white to buff precipitate formed. The mixture was allowed to reflux from its own heat of reaction. A stream of gas which decolorized bromine was evolved slowly. After standing twelve hours the mixture was worked up as usual. The product was fractionated at 740 mm. through Column I to give: (1) 13.6 g., 62–94°; (2) 11.5 g., 94-101°; (3) 8.2 g., 101–103°; (4) 92.3 g., 103–106°; (5) 23.0 g., 106–132°; (6) 11.4 g., 132-133" dec.; (7) 20 g. of black tarry residue. Fraction 4 was identified as pinacolone by m. p. and mixed m. p. determinations on its semicarbazone and 2,4-dinitrophenylhydrazone.[10] These points were 154–154.5° and 125.5–126°, respectively. The yield of pinacolone was 40.7% based on the Grignard reagent. Other runs have given somewhat higher yields. K. C. Laughlin of this Laboratory has obtained a 54% yield by this method.

Acetyl Chloride and Tertiary-amylmagnesium Chloride.—Two reactions were carried out, one in which the temperature of the reaction mixture was maintained at or below 0°, and one at the temperature of boiling ether.

Reaction at 0°.—To 172.7 g. (2.2 moles) of acetyl chloride dissolved in 400 cc. of dry ether was added with stirring 900 cc. of tertiary-amylmagnesium chloride solution containing 1.97 moles of Grignard reagent. The flask containing the acetyl chloride solution was immersed in a salt–ice freezing mixture. At one time the temperature of the mixture rose to +3°, but most of the time it was at −3° or below. A cream-colored precipitate formed. The mixture was stirred for half an hour at −2° after all the Grignard reagent was added and for another half hour with the cooling mixture removed. It was then decomposed on ice and treated as usual. The product was fractionated at 730 mm. through Column II to give: (1) 6.0 g., 68–120°; (2) 7.3 g., 120–125°, n_{D}^{20} 1.4038; (3) 25.7 g., 125-130°, 1.4066; (4) 24.7 g., 130–135°, 1.4100; (5) 16.1 g., 135–140°; 57.6 g. of residue. The desired methyl tertiary-amyl ketone was undoubtedly in the material boiling at 125–140° but no constant boiling point was obtained.

Reaction in Refluxing Ether.—To 196 g. (2.5 moles) of acetyl chloride dissolved in 600 cc. of dry ether was added with stirring during six and one-half hours 900 cc. of tertiary-amylmagnesium chloride solution containing 1.99 moles of Grignard reagent. The reaction was quite vigorous and the ether refluxed steadily. After 300 cc. of Grignard solution had been added, 50 g. (0.6 mole) of acetyl chloride was added to ensure an excess of chloride in the reaction mixture. A white precipitate formed. The reaction mixture stood overnight in the laboratory and was then filtered by suction The filtrate and precipitate were worked up separately.

The filtrate was poured on ice. There was no turbidity. The ether layer was separated and the aqueous portion extracted twice with small amounts of ether. The combined ether solutions were stirred for ten minutes with about one-fourth their volume of saturated aqueous potassium carbonate solution. The solution was light yellow in color. It was dried over 50 g. of anhydrous potassium carbonate for two hours and the ether was removed through a small partial condensation column. The product was fractionated at 738 mm. through Column II to give: (1) 5.5 g., 46-99°; (2) 5.0 g., 99-110"; (3) 19.9 g., 110–125°; (4) 9.4 g., 125–128°; (5) 12.0 g., 128–133°.

The precipitate was decomposed with ice in the usual way. The product was dried as usual and was fractionated at 737 mm. through Column II to give: (1) 3.5 g., 120–125°, n_{D}^{20} 1.4074; (2) 20.5 g., 125–129°, 1.4086; (3) 34.2 g., 129–132°, 1.4100; (4) 21.5 g., 132–137°, 1.4122; (5) 19.5 g., 137–160°; (6) 15 g., black tarry residue.

Purification of the Methyl Tertiary-amyl Ketone.—The 125–140° fractions from the

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(9) Whitmore and Badertscher, THIS JOURNAL, 64, 825 (1932).

(10) Allen, *ibid.*, 52, 2958 (1930).

three preceding fractionations were combined and steam distilled from aqueous potassium carbonate solution in order to remove the last traces of acetyl chloride. The ketone was salted out of the distillate with sodium chloride and separated. It was dried overnight with sodium sulfate at 0°. It was then fractionated at 721 mm. through Column I, giving 68.3 g. of product boiling at 129–131°. The semicarbazone melted at 138.5–139°. Wischnegradski[11] gives the boiling range of this ketone as 131.5–132.5° and Meerwein[12] reports the melting point of the semicarbazone as 136–138°.

A small sample of the ketone was oxidized with chromic acid. The amide of the high-boiling oxidation product (b. p. range 145–185°) was prepared. This was compared with the amide prepared from a known sample of ethyldimethylacetic acid; known and unknown and mixed m. p. 102.7–103.2° Haller and Bauer[13] give the melting point of this amide as 103–104°.

Acetyl Chloride and **Methyldiethylcarbinylmagnesium** Chloride.—A one mole run carried out in the usual way gave a product which on fractionation at 749 mm. through Column I gave the following: (1) 10.8 g., 36–63°; (2) 20.0 g., 63–65°, n_D^{20} 1.3870; (3) 17.8 g., 66–70°, 1.3989; (4) 17.8 g., 70–151°; (5) 21.9 g., 151–156°, 1.4206. Fraction 5 represented an 18% yield of 3-methyl-3-ethylpentanone-2 semicarbazone, m. p. 168.5–169°. Nybergh gives the boiling point of this ketone as 153.5° and the melting point of its semicarbazone as 168°.[14] Fraction 2 decolorized bromine.

Acetyl Chloride and **Dimethyl-*n*-butylcarbinylmagnesium** Chloride.—A one mole run was carried out in the usual way. The reaction was very vigorous. The dried product, fractionated at 743 mm. and at 20 mm., gave the following fractions: (1) 41 g., 35–41°; (2) 19.4 g., 41–81°; (3) 13.5 g., 81–90°, n_D^{20} 1.3900; (4) 28.6 g., 90–91°, 1.3950; (5) 26.2 g., 91–93° dec., 1.3986; (6) 13.1 g., 68–70.5° (20 mm.), 1.4206; (7) 8.9 g., 71–74° (20 mm.), 1.4218. Fractions 3–5 decolorized bromine. Fraction 6 represented a 9% yield of 3,3-dimethylheptanone-2, semicarbazone, m. p. 129–130°. Leers gives the boiling point of this ketone as 169.5° (735 mm.) and the melting point of its semicarbazone as 130°.[15]

Reactions of Tertiary Grignard Reagents **with** Formaldehyde.—The following tertiary Grignard reagents were treated with gaseous formaldehyde: dimethyl-*n*-amylcarbinyl-, methylethyl-n-propylcarbinyl-, methylethyl-n-butylcarbinyl- and triethylcarbinylmagnesium chloride.[16]

2,2-Dimethylheptanol-1 (from dimethyl-n-amylcarbinylmagnesium chloride and formaldehyde)—b. p. 88–89° (15 mm.), n_D^{20} 1.4339; yield, 40.7%, based on Grignard reagent.

Anal. Calcd. for $C_9H_{20}O$: C, 74.91; H, 13.98. Found: C, 74.70, 74.74; H, 13.75, 13.85.

2-Methyl-2-ethylpentanol-1 (from methylethyl-n-propylcarbinylmagnesium chloride and formaldehyde)—b. p. 75.5–76° (15 mm.), n_D^{20} 1.4353; yield, 30%, based on Grignard reagent.

Anal. Calcd. for $C_8H_{18}O$: C, 73.76; H, 13.92. Found: C, 73.76, 73.73; H, 13.70, 13.75.

2-Methyl-2-ethylhexanol-1 (from methylethyl-n-butylcarbinylmagnesium chloride and formaldehyde)—b. p. 85.5–86° (11 mm.), n_D^{20} 1.4401; yield, 31%, based on Grignard reagent.

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(11) Wischnegradski, *Ann.*, 178, 105 (1875).

(12) Meerwein, *ibid.*, 396, 256 (1913).

(13) Haller and Bauer, *Compt. rend.*, 148, 129 (1909).

(14) *Ber.*, 55B, 1960 (1922).

(15) Leers, *Bull. soc. chim.*, [4] 39, 651 (1926).

(16) *Cf.* Whitmore and Church, THIS JOURNAL, 55, 1119 (1933).

Anal. Calcd. for $C_9H_{20}O$: C, 74.91; H, 13.98. Found: C, 74.87, 75.06; H, 13.76, 13.91.

2,2-Diethylbutanol-1 (from triethylcarbinylmagnesium chloride and formaldehyde)—b. p. 75–78" (12 mm.), n_{D}^{20} 1.443; yield, 10%, based on Grignard reagent.

Anal. Calcd. for $C_8H_{18}O$: C, 73.76; H, 13.92. Found: C, 73.78, 73.54; H, 13.75, 13.64.

Reaction of Carbon Dioxide with Dimethyl-n-butylcarbinylmagnesium Chloride and with Dimethyl-n-amylcarbinylmagnesium Chloride.—No attempt was made to obtain the maximum yield of acids since the runs were small, and it has been our experience that the best yields of Grignard reagent are not obtained in small runs. K. C. Laughlin of this Laboratory has obtained a 42% yield of methyldiethylacetic acid in a 3-mole run, based on the methyldiethylcarbinyl chloride used.

Dimethyl-n-butylcarbinylmagnesium Chloride and Carbon Dioxide.—A half mole preparation of the Grignard reagent was made as usual. The total time for the halide–ether addition was four hours. Fifty cc. of ether was added and carbon dioxide was passed into the stirred mixture for five hours, pressure being applied by dipping the outlet tube of the apparatus into a 60-mm. column of mercury. The reaction flask was cooled by an ice–salt freezing mixture. The reaction mixture was decomposed by acidifying with 1:1 sulfuric acid. The ether layer was separated and the aqueous layer extracted ten times with 10-cc. portions of ether and the combined ether solutions dried over 30 g. of sodium sulfate in the refrigerator.

Suction (water pump) was applied and the ether removed. The amide was prepared from this crude acid in the usual way by heating a small portion with two or three times its volume of phosphorus trichloride until a pasty yellow solid commenced to precipitate and then decanting the mixture into cold aqueous ammonia. The amide was insoluble in water and was recrystallized by dissolving in ethyl acetate and precipitating with petroleum ether; m. p. of amide, 92.8–93.8° (uncorr.).

Dimethyl-n-amylcarbinylmagnesium Chloride and Carbon Dioxide.—A one-third mole preparation of the Grignard reagent was carried out in the usual manner. The mixture was diluted with 100 cc. ether, a salt–ice freezing mixture was placed around the reaction flask and carbon dioxide gas was passed into the flask with stirring, pressure being applied by dipping the outlet tube 80 mm. under the surface of mercury contained in a test-tube. The reaction mixture was decomposed and worked up in the same manner as in the preceding preparation. The ether was taken off through Column IV and the distillation continued until the temperature reached 115" at atmospheric pressure. The distillate consisted of olefins. The remaining olefin was removed by suction and the residue was fractionated at 10 mm. through Column IV to give: (1) 1.3 g., 110–117"; (2) 3.9 g., 117–118°, n_{D}^{20} 1.4335; (3) 4.9 g., 118°, 1.4318; (4) 3.2 g., 118–118.5°, 1.4305. Fractions 2-4 represented a 22% yield of dimethyl-n-amylacetic acid Its amide, prepared in the usual way, melted at 102.5–103.5°.

Summary

1. The yields of eight aliphatic tertiary organomagnesium chlorides have been determined. These range from 60 to 80%.

2. The reaction between tertiary Grignard reagents and ethyl chlorocarbonate gives the ethyl ester of the corresponding substituted acetic acid. This reaction is useful synthetically.

3. Tertiary-butylmagnesium chloride reacts with ethyl carbonate to form ethyl trimethylacetate. Higher tertiary Grignard reagents react little or not at all with ethyl carbonate.

4. Tertiary-butylmagnesium chloride, when added to an excess of acetyl chloride in ether, gives pinacolone in good yields. The yields of the corresponding ketones from higher tertiary Grignard reagents and acetyl chloride are lower.

5. Four homologs of neopentyl alcohol, 2,2-dimethylheptanol-1, 2-methyl-2-ethylpentanol-1, 2-methyl-2-ethylhexanof-1, and 2,2-diethylbutanol-1 have been prepared from the action of formaldehyde with tertiary Grignard reagents.

6. Preliminary studies have been made on the action of carbon dioxide with certain higher tertiary Grignard reagents.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. II[1]

BY R. W. BEATTIE[2] AND FRANK C. WHITMORE

The conversion of simple mercurated organic compounds of the type, RHgX, to the mercuri-bis type, R_2Hg, has long been of interest.[1] In the present work this change has been produced in a large number of aromatic mercury compounds by means of sodium alcoholates and alcoholic potassium hydroxide[3] and by means of a long known but neglected reagent for this purpose, namely, sodium cyanide.[4] These studies have been conducted with the chloronaphthylmercuric chlorides prepared from a series of new chloronaphthalene sulfinic acids obtained from the chloronaphthalene sulfonyl chlorides made available in this Laboratory in another research.[5] The diarylmercury compounds were converted to the arylmercuric bromides and iodides by treatment with mercuric bromide and iodide.

Experimental

A. Mercury Compounds of the Chloronaphthalenes

The Chloronaphthalene Sulfinic Acids.—Of the various ways of converting sulfonyl chlorides to sulfinic acids,[6] the sodium sulfite method was adopted for the present work. In place of the sodium bicarbonate usually recommended an equivalent amount of dilute sodium hydroxide solution was used. The preparation of 1-chloronaphthalene-6-sulfinic acid may be taken as typical.

A solution of 400 cc. of water, 25.2 g. (0.2 mole) of sodium sulfite, 80 cc. of 20% sodium hydroxide solution (0.4 mole) was heated to boiling in a 1-liter beaker equipped

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(1) Whitmore and Sobatzki, THIS JOURNAL, 55, 1128 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degtee.

(3) Whitmore, Hanson and Carnahan, THIS JOURNAL, 51, 894 (1929).

(4) Buckton, Ann., 108, 105 (1858).

(5) Beattie and Whitmore, THIS JOURNAL, 55, 1546 (1933).

(6) "Organic Syntheses," 2, 90 (1922).

with a mechanical stirrer. To the stirred solution just below the boiling point was added gradually 52 2 g. (0.2 mole) of finely powdered 1-chloronaphthalene-6-sulfonyl chloride.[5] The mixture was filtered and the hot filtrate was acidified. After cooling, the sulfinic acid precipitate was filtered off, washed and dried in vacuum over phosphorus pentoxide; yield 44 g., 95%. Six other runs gave an average of 91%. The melting point of the freshly prepared substance was 127–128". On long standing the melting point gradually rose as high as 250°. The work on the sulfinic acids is summarized in Table I. All of these are new except the 1,5 compound which was reported by Reissert as decomposing above 220°.[7]

TABLE I

CHLORONAPHTHALENE SULFINIC ACIDS

Position of Cl and SO_2H	M. p.,[a] °C.	Yield, %[b]	G. made	Cl analyses Calcd.: 15.6 Found[c]
1,4	111	91	83	15.4
1,5	121	65	72	15.5
1,6	127–128	91	210	16.1
1,7	128.5–129	77	110	16.0
1,8	105[d]	97	65	16.0
2,1	87[d]	88	260	15.5
2,6	[e]	90	320	15.7
2,7	134	94	220	16.2
2,8	127	82	40	15.4

[a] The melting points are of freshly prepared dry samples. In several cases long storage even in tightly stoppered bottles produced increases in m. p. of over 100". This phenomenon was not studied. [b] Yield based on the pure sulfonyl chloride used. [c] The figures given are the average of at least two analyses in each case. [d] The 1,8 and 2,1 acids darkened rapidly when exposed to light. The latter even decomposed slowly when stored in a dark bottle. All of these sulfinic acids darkened slowly in direct sunlight. [e] Even a freshly prepared sample did not melt at 300°.

The sulfinic acids were soluble in acetone, alcohol, benzene and toluene but sparingly soluble in chloroform and carbon tetrachloride. Cold concentrated sulfuric acid gave a blue or purple color with the following acids, 1,4, 1,5, 2,1 and 2,8, and a green color with the 1,6, 1,7, 1,8, 2,6 and 2,7. A little time was sometimes necessary to develop the green color.

The Chloronaphthylmercuric Chlorides.—These were prepared by the reaction of Peters by boiling the sulfinic acids with aqueous mercuric chloride.[8] In the preparation of the 1,6 and 1,7 compounds the evolution of sulfur dioxide was very slow while the 1,8 and 2,1 sulfinic acids reacted very rapidly. The nine chloronaphthylmercuric chlorides were insoluble in most solvents except hot xylene, the 1,8 and 2,1 compounds being the most soluble and the 2,6 and 2,7 compounds the least soluble. With the exception of the 2,1 compound they formed white fluffy crystals which usually had a distinct static charge. The 2,1 compound formed fairly large dense plate crystals of a yellowish-white.

The Mercuri-bis-chloronaphthalenes.—These were prepared from the —HgCl compounds by treatment with an excess of alcoholic sodium iodide.

They were also prepared by the new method using an excess of alcoholic sodium cyanide. In each case the nature of the diarylmercury compound was proved by its reaction with mercuric chloride in acetone to give the original chloronaphthylmercuric chloride. In a similar way the new chloronaphthylmercuric bromides and iodides were prepared.

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(7) Reissert, Ber., 55, 873 (1922).

(8) Peters, "Organic Syntheses." 3, 99 (1923); *Ber.*, 38, 2567 (1905)

TABLE II

MERCURY COMPOUNDS OF THE CHLORONAPHTHALENES

	ArHgCl				Ar_2Hg				ArHgBr				ArHgI			
			Analysis Hg calcd.: 50.5 Cl calcd.: 17.8 Found				Analysis Hg calcd.: 38.3 Cl calcd.: 13.5 Found				Analysis Hg calcd.: 45.4. Cl + Br calcd.: 26.1 Found:				Analysis [e]Hg calcd.: 41.0 Cl + I calcd.: 33.2 Found:	
Position Cl and Hg	M. p.[g]	Yield,[a] %	Hg[b]	Cl[c]	M. p., °C.	Yield,[d] %	Hg[b]	Cl[c]	M. p., °C.	Yield,[e] %	Hg[b]	Cl + Br[c]	M. p., °C.	Yield,[e] %	Hg[b]	Cl + I[c]
1,4	252	69	50.7	18.2	275.5	78	38.4	13.3	251	86	45.6	26.5	233	84	41.3	33.8
1,5	244	83	50.3	18.1	223.5	84	38.5	13.8	231.5	96	45.4	26.4	221.5	87	41.1	33.0
1,6	307	48	50.9	17.6	246	74	38.4	13.7	316	83	45.7	25.6	276.5	82	41.3	33.1
1,7	223	50	50.7	18.1	230.5	95	38.3	13.2	247	81	45.8	26.6	257	76	41.3	33.7
1,8	214	84	50.6	18.3	215.5–216.5	80	38.4	13.7	195.5	89	45.8	26.0	156.5–157.5	86	41.5	32.9
2,1	215	91	50.6	18.3	293.5	40	38.2	13.3	204	74	45.9	26.4	[h]			
2,6	260	42	50.3	18.2	260[f]	77	37.8	13.0	260	81	45.3	25.9	298	82	41.2	32.9
2,7	295	56	51.0	18.1	299	84	38.0	13.7	288	76	45.6	25.9	272	74	41.3	32.8
2,8	232.5	83	50.9	17.5	272.5	83	38.3	13.4	226	69	45.5	26.3	192.5	76	41.5	32.7

[a] Yield based on the sulfinic acid used. [b] The mercury analyses were made by iodimetry by the method developed by Ehrenfeld and Sobatzki [Whitmore and Sobatzki, THIS JOURNAL, **55** 1128 (1933)]. The figures recorded are the average of two analyses. [c] Average of two analyses. [d] Yield based on the chloromercuri compound using the sodium iodide method. The sodium cyanide method gave slightly lower yields. [e] Yield based on the mercuri-bis compound used. [f] This was the most insoluble of the mercuri-bis compounds. [g] The chloromercuri compounds prepared from the sulfinic acids were checked with those prepared from the mercuri-bis compounds and mercuric chloride. In a few instances the latter process gave slightly purer substances. Mixed m. p. determinations were made in all cases. [h] The 2,1 compound was not made because of lack of material at the end of the research.

In several cases the melting points of the mercuri-bis and chloromercuri compounds were nearly the same. In such cases mixed melting points were used to detect the difference in the compounds. In six out of the nine cases the melting point of the mercuri-bis compound was distinctly higher than that of the corresponding chloromercuri compound. The mercuri-bis compounds formed white minute needles except the 1-mercuri-bis-2-chloronaphthalene and 8-mercuri-bis-1-chloronaphthalene which formed dense white powders.

The Bromomercuri **and** Iodomercuri Compounds.—Most of the bromomercuri-compounds crystallized from the acetone reaction mixture. The 1,6, 2,6 and 2,7 compounds were insoluble in hot acetone and were crystallized from hot xylene as fine white powders. The 1,4 compound crystallized from hot acetone in small golden plates and the 1,2 compound in very dense yellow plates. The others formed white fluffy needle crystals.

The iodomercuri compounds have properties similar to the bromo compounds. The 1,6, 1,7, 2,6 and 2,7 compounds had to be crystallized from hot xylene because of their insolubility in acetone. The 2,7 compound was obtained in small nacreous plates and the 2,8 compound as golden plates. The others formed fine white needles.

The work on the new mercury compounds is summarized in Table II.

B. The Formation of Mercuri-bis Compounds by **Alkali** Cyanides

Phenyl Compounds.—Phenylmercuric chloride, m. p. 251°, was prepared from aniline in 23% yields by the method of Nesmejanow.[9] Phenylmercuric acetate, m. p. 145–146°, was prepared by the mercuration of benzene with mercuric acetate in alcohol solution.[10]

A solution of 1.3 g. (2 mols) of potassium cyanide in 100 cc. of 95% alcohol was refluxed with 3.12 g. (1 mol) of phenylmercuric chloride for one hour. On cooling 1.37 g. of pure diphenylmercury, m. p. 123–123.5°, separated, a yield of 38%. This reaction is in sharp contrast to the failure of a similar experiment with sodium iodide to give mercury diphenyl.[1] Similar results were obtained with phenylmercuric acetate and 2 or 3 mols of potassium or sodium cyanide. The use of only 1 mol of the cyanide gave phenylmercuric cyanide. m. p. 204–205°, in 85% yield. The same result was obtained with phenylmercuric acetate.

p-Tolyl Compounds.—Di-p-tolylmercury, m. p. 243–244°, was obtained in 73% yield by the action of an alcoholic solution of 3 mols of sodium cyanide on p-tolylmercuric chloride.

Naphthyl Compounds.—α-Naphthylmercuric chloride, m. p. 189–190°, was obtained in 20% yield from α-naphthylamine.[9] The @-compound, m. p 267°, was made in 80% yield from sodium naphthalene-2-sulfinate (Peters) and in 47% yield from β-naphthylamine (Nesmejanow).

TABLE III

PREPARATION OF DI-β-NAPHTHYLMERCURY

Reagents	Solvent	Conditions	M. p. of product, °C.	Yield, %
$ArHgCl + 2$ mols NaI[a]	Alcohol	Boil, 15 hrs.	238–239	86
$ArHgCl + Cu$[b]	Pyridine	Boil, 1 hr.	244	70
$ArN_2Cl.HgCl_2 + Cu$	Acetone	Cold, 1 hr.	241–242	40
ArHgCl $ 3 mols NaCN	Alcohol	Boil, 0.5 hr.	247–248	83.5
$ArHgCN + 2$ mols $NaCN$	Alcohol	Boil, 0.5 hr.	246–248	

[a] *Cf.* Steinkopf's results with the α-compound, *Ann.*, 413, 329 (1917). [b] Hein and Wagler, *Ber.*, 58, 1499 (1925).

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(9) Nesmejanow, *Ber.*, 62, 1010 (1929).

(10) Sneed and Maynard, THIS JOURNAL, 44, 2942 (1922).

Di-β-naphthylmercury was made in a variety of ways. The best method was that using sodium cyanide. The results are summarized in Table III.

The β-naphthylmercuric cyanide used in the last experiment melted at 213–214° and was made by the action of 1 mol of cyanide with the naphthylmercuric chloride.

The di-β-naphthylmercury reacted with mercuric bromide and iodide in boiling acetone to give nearly quantitative yields of β-naphthylmercuric bromide, m. p. 266–266.5° and of β-naphthylmercuric iodide, m. p. 251–251.5°.

Chloronaphthyl Compounds—Each of the nine chloronaphthylmercuric chlorides was converted to the corresponding mercuri-bis compounds by treatment with 3 mols of sodium cyanide in boiling alcohol. In several cases products with melting points higher than those obtained by the sodium iodide method resulted. The yields, however, were usually slightly lower by the cyanide method.

C. The Formation of Mercuri-bis Compounds by Alcoholates and Alcoholic Alkalies

The arylmercuric chlorides were refluxed with an excess of the alcoholic reagent. The results appear in Table IV. The method is general but is inferior to the older methods.

TABLE IV

ArHgCl	Reagent	Solvent	Time of refluxing	M. p. Ar_2Hg, °C.	Yield. %
Phenyl	CH_3ONa	Abs. CH_3OH	3 hrs.	123.5	34
p-Tolyl	C_2H_5ONa	Abs. C_2H_5OH	3 hrs.	244	59
p-Tolyl	C_2H_5ONa	95% C_2H_5OH	3 hrs.	244	41
p-Tolyl	$(CH_3)_2CHONa$	$(CH_3)_2CHOH$	3 hrs	244	45
β-Naphthyl	C_2H_5ONa[a]	Abs. C_2H_5OH	[a]	242–244	57 to 77[a]
β-Naphthyl	C_2H_5ONa	95% C_2H_5OH	[b]	241–246	48–62[b]
β-Naphthyl	CH_3ONa	Abs. CH_3OH	3.5 hrs.	244	50
β-Naphthyl	$(CH_3)_2CHONa$	$(CH_3)_2CHOH$	3.5 hrs.	247	42
β-Naphthyl	KOH[c]	Abs. C_2H_5OH	3–7 hrs	245	48–62

[a] A series of nine experiments with varying amounts of alcoholate and varying conditions was tried. Less than 2 mols of alcoholate gave impure products. Larger amounts gave no increase in the yields. Refluxing or stirring at room temperature for seven hours gave about the same yield. The method is not as good as the iodide or cyanide method. [b] A series of four experiments. [c] A series of five experiments. Less than 3 mols of potassium hydroxide was ineffective and more gave no increase in yield.

Summary

1. Eight chloronaphthalene sulfinic acids have been prepared for the first time and new data have been obtained for the 1,5 compound.

2. Thirty-five new organic mercury compounds related to the chloronaphthalenes have been prepared. Di-β-naphthylmercury has been obtained with m. p. 247–248°.

3. Equivalent quantities of alkali cyanides convert arylmercuric chlorides to the arylmercuric cyanides but an excess of alkali cyanide gives the diarylmercury compounds. The products are purer but the yields are somewhat lower than with the iodide method for preparing these substances.

4. Sodium alcoholates and alcoholic potassium hydroxide also form the diarylmercury compounds but in yields distinctly lower than those of the iodide and cyanide methods.

STATE COLLEGE, PENNSYLVANIA

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

The Thermal Decomposition of Phenyl Vinyl Ether

BY WALTER M. LAUER AND MARVIN A. SPIELMAN

In connection with a general study of the molecular rearrangements of the alpha, beta-unsaturated ethers it became necessary to examine the behavior of phenyl vinyl ether on thermal decomposition. Powell and Adams[1] have reported that the principal product of the reaction is phenol. Our results have led us to believe that although phenol plays a part in the reaction it always appears in the end-products in relatively small amounts.

A sample of phenyl vinyl ether was heated in a sealed tube as described in the reference cited, and on distillation essentially the same fractions were obtained. It was observed, however, that a large part of the high-boiling material was insoluble in aqueous alkali. In subsequent experiments the reaction mixture was extracted with alkali and then distilled under diminished pressure. From a 20-g. sample, the alkali extract never contained more than half a gram of phenol isolated as tribromophenol. The balance of the product gave on distillation a large portion of unchanged starting material and 2–6 g. of a colorless oil which boiled at 154–155° at 14 mm.; approximately an equal amount of tarry residue always remained.

The colorless oil was shown to have the empirical formula $C_{14}H_{14}O_2$. It was insoluble in aqueous alkali, but with bromine water it gave a bulky precipitate of tribromophenol, and on oxidation with nitric acid, the only product isolated was 2,4-dinitrophenol. Hydrolysis gave phenol and acetaldehyde. The physical and chemical properties seemed to correspond to acetaldehyde diphenylacetal as described by Fosse.[2] A sample was therefore prepared by his method and the compounds were found to be identical.

The tarry residue remaining after the distillation could not be induced to crystallize or sublime. The apparent molecular weight was found to be 806, although the figure is perhaps much too low, due to included impurities.

The presence of acetaldehyde diphenylacetal in the decomposition products of phenyl vinyl ether is difficult to explain, although a reasonable mechanism by which it might be formed involves the addition of phenol to the unchanged starting material. $C_6H_5OH + C_6H_5OCH{=}CH_2 \longrightarrow CH_3\text{-}CH(OC_6H_5)_2$. That hydroxy compounds add to alpha,beta-unsaturated ethers is well known, but to ensure the plausibility of the reaction in this case, a mixture of phenyl vinyl ether and phenol was heated in a sealed tube under the usual conditions of the decomposition reaction. The unexpected result was that all of the phenyl vinyl ether was destroyed; from the tarry mixture only phenol could be isolated and in greater amounts than had

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(1) Powell with Adams, THIS JOURNAL, **42**, 646 (1920)

(2) Fosse, *Bull. soc. chim.*, [3] **23**, 515 (1900)

been added. This seemed to point to the instability of acetaldehyde diphenylacetal in the presence of relatively large amounts of phenol at high temperatures, a supposition which was confirmed by heating the two substances together to 260°. The result was the same as in the preceding experiment. However, by slowly adding phenol to boiling phenyl vinyl ether during *a* period of several hours, a smooth addition took place and the corresponding acetal was formed in 90% yield.

The origin of the phenol is not clear, although it is probably connected in some way with the polymeric material which always appears as a side product.

Experimental Part

The phenyl vinyl ether used in this work was prepared by the following set of reactions

$$C_6H_5OH \xrightarrow[KOH]{ClCH_2CH_2OH} C_6H_5OCH_2CH_2OH \xrightarrow{SOCl_2} C_6H_5OCH_2CH_2Cl \xrightarrow{KOH} C_6H_5OCH{=}CH_2$$

Although yields were not large, the nature of all reagents made the synthesis more satisfactory than others in the literature.[3]

β-Chlorophenetole.—Two moles each of potassium hydroxide, phenol and ethylene chlorohydrin, 350 cc. of water and 400 cc. of benzene were placed in a two-liter flask under a reflux condenser and boiled on a steam-bath for twelve hours. The benzene layer was separated, washed free of phenol with 5% sodium hydroxide and dried by boiling off about one-third of the benzene. It was added slowly through a dropping funnel set in a reflux condenser to 2 moles of practical grade thionyl chloride in an equal volume of benzene. The solvent was evaporated and the product was distilled at atmospheric pressure under a hood; yields were consistently 50–53%; b. p. 213–221°.

Phenyl Vinyl Ether.—This was prepared in 50% yield by twice distilling the crude β-chlorophenetole from powdered potassium hydroxide in the manner previously described by the present authors.[4] It boiled at 154–158° and redistillation gave 155–156°, the value in the literature.

Thermal Decomposition of Phenyl Vinyl Ether.—The following typical run is given in detail. All others were similarly performed with differences only in time and temperature.

Twenty-five grams of phenyl vinyl ether was sealed in a soft glass Carius tube and heated to 295–300° for three hours. The tube was allowed to cool, and on unsealing no pressure was observed. The product was clear and only slightly discolored. It was taken up in ether and extracted twice with 50-cc. portions of 5% sodium hydroxide. This extract brominated gave 0.7 g. of tribromophenol, m. p. and mixed m. p. 90–91°, indicative of about 0.3 g. of phenol. The ether solution was evaporated and distilled under diminished pressure. The first fraction was 4.5 g of unchanged starting material which came over below 70° at 14 mm. An intermediate fraction of 3.8 g. distilled as the temperature rose steadily to 153°. The principal fraction, 8.6 g., was collected at 153–156". A tarry residue remained.

By working over the second and third fractions, 8 g. of pure acetaldehyde diphenylacetal was obtained; b. p. 154–155° at 14 mm., 174–175° at 26 mm.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5. Found: C, 78.6, 78.6; H, 6.5, 6.6.

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(3) Wohl and Berthold, *Ber.*, **43**, 2175 (1910); v. Braun and Kirschbaum, *ibid.*, **63**, 1399 (1920).

(4) Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931).

A sample was prepared according to the directions of Fosse[2] and the boiling points were found to be the same. On cooling with solid carbon dioxide both crystallized; m. p. and mixed m. p. 9–10'.

The usual run of 20 g. of phenyl vinyl ether heated to 260–280° for twelve hours gave 0.11 g. of phenol and 2.0 g. of the acetal. In no case was the amount of phenol isolated more than one-tenth of the yield of acetal.

Addition of Phenol to Phenyl Vinyl Ether.—Eight grams of phenyl vinyl ether was heated to boiling in an atmosphere of carbon dioxide. To this was added dropwise during eight hours 5 g. of phenol in 2 g. of phenyl vinyl ether. Boiling was continued for eight hours as the temperature (thermometer in liquid) rose slowly to 210°. The product was distilled and 10.4 g. of acetaldehyde diphenylacetal was collected at 172–178° at 26 mm.

Summary

Phenyl vinyl ether has been shown to decompose at 260–300° to give phenol, acetaldehyde diphenylacetal and an unknown substance of high molecular weight.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

Isomorphism and Alternation in the Melting Points of the Normal Alcohols, Acetates, Bromides, Acids and Ethyl Esters from C_{10} to C_{18}

BY JANE DICK MEYER AND E. EMMET REID

The alternation of properties, particularly melting points, in various series has engaged the attention of many investigators.[1,2,3] When the melting points of the normal alcohols are plotted against the number of carbon atoms a decided alternation is evident in the lower members but becomes so small for the higher that the scattered data in the literature are not sufficiently accurate and consistent to show whether it exists or not.

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(1) (a) Timmermans, *Bull. soc. Jim. Belg.*, **30**, 89–97; 31, 389 (1922); 36, 276–288 (1926); 38, 295 (1929); (b) Deffet, *ibid.*, 40, 385–402 (1931); (c) Cuy, THIS JOURNAL, 42, 503 (1920); (d) Pauly, *Z. anorg. allgem. Chem.*, 119, 271–291 (1922): (e) Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072–2094 (1931); (f) Gamer and Randall, *J. Chem. Soc.*, **125**, 881 (1924); (g) Garner, Madden and Rushbrooke, *ibid.*. 2491 (1926); (h) Garner and Rushbrooke, *ibid.*, 1351–1359 (1927); (i) Garner and King, *ibid.*, 1849–1861 (1929); (j) King and Garner. *ibid.*, 578–580 (1931); (k) Malkin, THIS JOURNAL, 62, 3739 (1930); (l) Malkin, *Nature*, 127, 126–127 (1931); (m) Malkin, *J. Chem. Soc*, 2796–2805 (1931); (n) Piper and Malkin, *Nature*, **126**, 278 (1930); (o) Whitby, *J. Chem. Soc.*, 1458 (1926); (p) Levene, West and Van der Scheer, *J. Biol. Chem.*, 20, 521–534 (1915); 23, 72; (q) Levene and Taylor, *ibid*, 69, 905–921 (1924); (r) Shepard, Henne and Midgley, THIS JOURNAL, 63, 1948–1958 (1931); (s) Deese, *ibid.*, 63, 3673–3682 (1931); (t) Verkade and Coops, *Rec. trav. chim*, 46, 903–917 (1927); (u) Blau, *Monatsh.*, 26, 103 (1905); (v) Krafft, *Ber.*, 16, 1714 (1882); (w) Gascard, *Compt vend.*, 170, 886–888, 1326–1328 (1920); *ibid.*, 163, 1484–1487 (1911); *Ann. chim.*, [9] 18, 347 (1921); (x) Bleyburg and Ulrich, *Ber.*, **64**, 2504–2513 (1913).

(2) Talvitie, *Ann. Acad. Sci. Fennicae*, No. 16, **A26**, 1–94 (1927).

(3) (a) Blaise and Gueriu, *Bull. soc. chim.*, [3] 29, 1903 (1903); (b) Jeffreys, *Am. Chcm. J.*, **22**, 14 (1899); (c) Slotta and Jacobi, *J. prakt. Chem.*, [2] 120, 249 (1929); (d) Fridau, *Ann.*, 83, 1 (1852); (e) Oskerko, *J. Russ. Phys.-Chem. Soc.*, 46, 413 (1914); *Chem. Zentr.*, II, 1264 (1914); (I) Youtz, THIS JOURNAL, 47, 2252 (1925); (g) Vorländer and Selke, *Z. physik. Chem.*. 129, 435 (1927); (h) Piper and co-workers, *Biochem. J.*, 26, 2072 (1931).

It seemed desirable to decide this question by preparing the normal alcohols from decyl to octadecyl in the highest purity practicable and determining their setting points by the most accurate method, using the same apparatus and temperature scale for all. For comparison the setting points of the acids and their ethyl esters, from which the alcohols were prepared, have been determined and also those of the bromides and acetates made from the alcohols. The melting points of many of these compounds, particularly those with uneven numbers of carbon atoms, were unknown.

In determining the setting point of cetyl alcohol a break in the cooling curve betrayed a transition in the solid state. This led to a study of the cooling curves for the other compounds and the discovery of polymorphism in a number of them. Garner and co-workers[1f,g,h,i] have studied polymorphism in the acids by cooling curves, Francis, Piper and Malkin[4] by x-rays and Malkin[1k] by x-rays and optical methods. Huffman, Parks and Barmore[5] and Garner, van Bibber and King[6] find transitions in a number of hydrocarbons by thermal measurements. Deese[1s] found a transition in n-amyl bromide and Levene and Taylor[1q] speak of two forms of the nitriles.

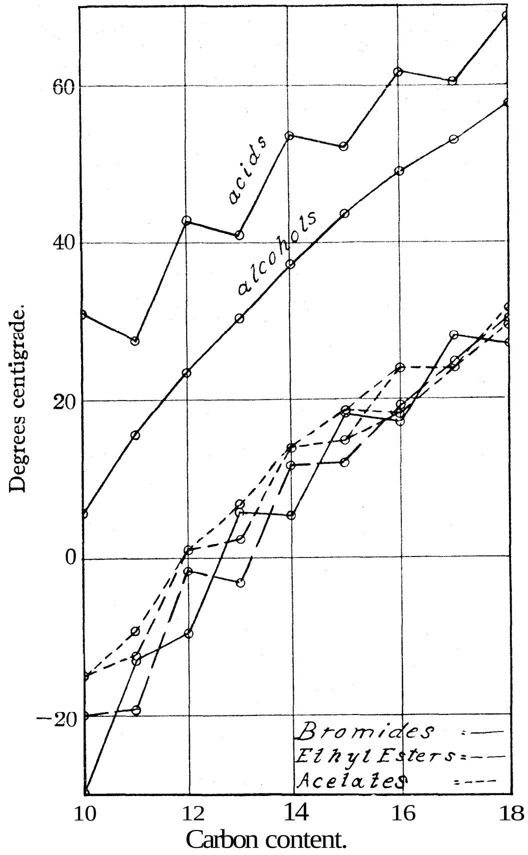

Fig. 1.—Melting points.

When our work was almost finished, Phillips and Mumford[7] published a paper on dimorphism of several of these compounds. They considered only cetyl and octadecyl alcohols and related compounds and also ethyl heptadecoate. They found two types of dimorphism. Some of their

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(4) Francis, Piper and Malkin, *Proc. Roy. Soc.* (London), **128A,** 214–252 (19301.

(5) Huffman, Parks and Barmore, THIS JOURNAL, **53,** 3876–3888 (1931).

(6) Garner, van Bibber and King, *J. Chem. Soc*, 1533 (1931).

(7) Phillips and Mumford, *ibid.*, 1732 (1931).

compounds showed two distinct melting points corresponding to two crystal forms, while others showed a break in the cooling curve of the solid indicating a change in crystal structure. This was enantiotropic and could be observed in either a cooling curve or a melting curve of the solid, When two distinct melting points were obtained, the crystal which formed first and had the lower melting point was designated as an "alpha crystal," while that which formed second, having a higher melting point, was termed a "beta crystal." For an arrest in the cooling curve of the solid they used the term "gamma modification." For the sake of clearness this convention will be followed here. They found alpha and beta crystals for cetyl chloride, cetyl and octadecyl acetate, ethyl palmitate and stearate, and diethyl cetyl malonate. No dimorphism was found in cetyl bromide, or iodide, n-hexadecane or ethyl cetyl ether. Transitions of the gamma type appeared in cetyl alcohol and ethyl heptadecoate.

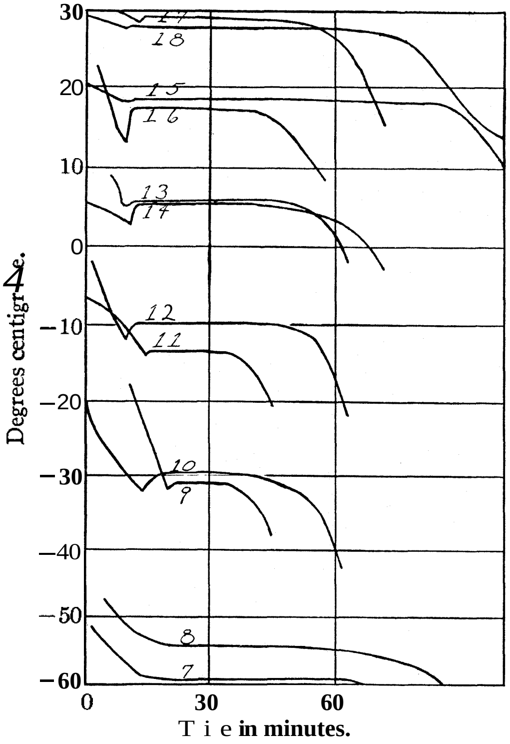

Fig. 2.—Bromides.

Since our work was finished (November, 1931), Malkin[1m] has published a paper on the ethyl esters in which he finds enantiotropic dimorphism in ethyl heptodecoate and higher uneven ethyl esters and Phillips and Mumford[8] have published a second paper considering the even esters C_{10}, C_{12}, C_{14} and C_{16} and C_{18} with one uneven ester, ethyl heptodecoate. They found no dimorphism for the lower even esters except ethyl myristate, for which they record an alpha fusion point of **11.7'** and a beta melting point of **12.3'**.

Smith[9] also studied dimorphism in ethyl palmitate, ethyl stearate and butyl stearate, the first two of which give alpha and beta crystals while butyl stearate gives only one kind. In a very recent paper[10] he discusses cetyl and octadecyl iodides and hexadecane and octadecane. From cool-

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(8) Phillips and Mumford, *J. Chem. Soc.*, 898 (1932).

(9) Smith, *ibid.*, 804 (1931).

(10) Smith, *ibid.*, 737-741 (1932).

ing curves of the pure solids he does not find any evidence of polymorphism but from binary systems he finds indications of a transition in these compounds.

Results

Alternation.—The results obtained are brought together in Table I and in figures.

TABLE I

FUSION POINTS AND CRYSTAL FORMS, °C.

Carbon content	Alcohols—a Form stable a Form (f. p)	Transition	Ref.	Bromides, fusion point	Ref	Acetates a Form (f p)		Transition	β Form (f. p.)	Ref.
10	5 99		9	– 2962		–15 05	S			
11	1585		10	–13 15		–12 59	M	Monotropic	–9.27	
12	23 87		11	– 9 6 0		1 13	S			
13	30 63	E 27 96–28 75	12	5 94		2 44	M	Monotropic	7.03	
14	37 62	E 34.58–35 33	13	5 67		14 01	S			20
15	43 84	E 37.33	14	18 63		14 99	M	Monotropic	18.77	
16	49 27	E 42.75–44 84	15	17 54	18	18 49	M	Monotropic	24.12	21
17	53 31	E 45 55–45 85	16	28 40		24 39	S			
18	57 85	E 51.93–52 89	17	27 35	19	29 97	M	Monotropic	31.95	22

Carbon content	Acids—a Form stable a Form (f. p)	Transition	Ref.	Hydrocarbons		a Form (f p)		Transition	β Form (f p)	Ref.
10	31.19		23	–29.76		–19.96	S			32
11	277.77	E 10.65–10 52	24	–25.65		–19.39	S			
12	43 22		25	– 9.73		– 1 6 8	S			33
13	41.55	E28.09–2759	26	– 6 2		– 3 13	S	E –11.94 to –12.26		
14	53.86		27	5 5		11 93	S			34
15	52.26	E 41.33–40.86	28	10		12 21	S	E 8 44–8.24		
16	61 82		29	18 2		19.72	M	Monotropic	23 2[a]	35
17	60.66	E 58.15	30	22.5		25.11	S	E 17 04–16.23		36
18	68.82		31	27.90		30 56	M	Monotropic	32 9[a]	37

[a] Data taken from Phillips and Mumford. E = enantiotropic, S = stable, M = metastable.

The numbers refer to prior references, the letters to Ref. 1 (a = 1a; b = 1b, etc.). [9] 6.4° t and u; 7° 2. [10] 16.3° t; 11° z; 19° u and 3b. [11] 23.8° t; 24–26" u; 24° v; 23° k. [12] 30.5° u. [13] 37.7° h; 38° v, u and k. [14] 44° w; 45–46° u and 10. [15] 49.1° 5; 49° w and k; 49–49.5° u; 49.27° 8 and v. [16] 54° p and w. [17] 58.5° p and w; 59° v and k; 57.95" 8; 58.5–59.5° q. [18] 16.3° 5; 15–16" 3c; 15" 3d. [19] 28.5" 3e [20] 12–13° v. [21] 22–23° v; 22.7° 3f; α 18.7°, β 22.3° 5. [22] 31° v; α 29.7°, β 31.3° 5. [23] 31.3° b; 31.4" g; 31° 3g and u. [24] 26° 3b; 28.4°, g; 28.2°, i; 28° u. [25] 43° u; 43.7°, g. [26] 40.5" u, 41.6° g; 41.0° i; 44.5–45.5° p. [27] 54° u, 2 and 3h; 53.7° g. [28] 52.1' 2 and g; 52" h; 51° u; 52.5" 3h. [29] 63.1" 2; 62.7" g; 62° u and 3g; 69.41' 7 and 8. [30] 62.0" 2; 61.4° g; 60.7° i; 60 u. [31] 70.1 2; 70.65° g; 69° u and 3g; 69.41" 7 and 8. [32] —20.5' 5; —19.9" b. [33] —2.0° 5; —10° u. [34] 11.0° b; 10.5–11.5' u; α 11.7°, β 12.3° 5. [35] α 19.2° 5; 19.4° 7 and 8; β 23.2° 5; 24.8° 7 and 8; 24° 3g; 25° 2; 24.2° u. [36] 25.2° 5; 25° 1 and m; 28° 2; 27° u. [37] α 30.4' 5; 30.92' 7 and 8; β 32.9" 5; 33.4' 7 and 8; 34° 2; 33.7° u; 33–34 q; 33° 3g.

From butyl to decyl the melting points of the even alcohols are on a slightly higher curve than those of the odd. This seems to continue with the higher alcohols but in spite of all our care the accuracy of our measurements is hardly great enough to make sure of this.

We have inserted in our table the melting points of the hydrocarbons as given in the literature. It is a remarkable fact that the even bromides and the hydrocarbons from which they are derived have almost the same melting points. It may be said that, as far as the melting point is concerned, a terminal bromine atom has the same effect as a methyl group since if the curve for the alkyl bromides were moved one space to the right it would almost coincide with the hydrocarbon curve. In the bromide series the alternation is the reverse of what it is in the others, the odd compounds having the high melting points. Beginning with C_{13} the odd melt higher than the next higher even.

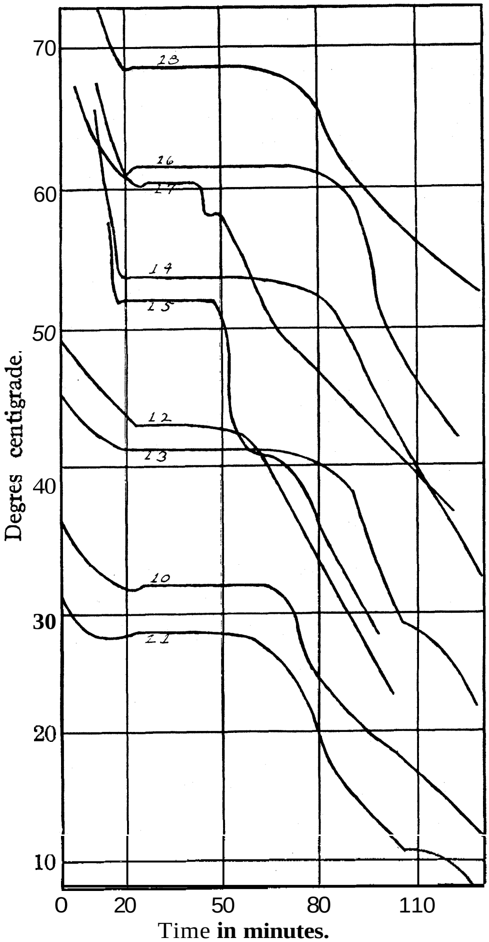


Fig. 3.—Acids.

The curve for the acetates is double since there are two forms for those of C_{11}, C_{13}, C_{15}, C_{16} and C_{18}. The melting points of the acetates and the isomeric ethyl esters are on very similar curves, both showing alternation. The differences between the melting points of the isomers show alternation but diminish as we go up the series; the acetates melt higher as far as C_{15}. For ethyl palmitate and stearate we obtained only the low melting forms but have plotted the data of Phillips and Mumford for the high.

Polymorphism.—From the time–temperature curves of the bromides, it is evident that there is no polymorphism. A transition was observed (Fig. 3) in the odd acids even during their preparation When one of these acids in the molten condition is poured into water and cooled it first forms a solid cake, as the even acids do, but soon this would disintegrate with the formation of small, apparently denser, crystals which would remain suspended in the water. An uneven acid cooled in a glass container breaks away from the walls.

The cooling curves for the acids are reproduced in Fig. **2.** The transition temperature of margaric acid is near its setting point but this interval increases as we go down the series.

The polymorphism of the alcohols is shown in their cooling curves.

Decided arrests were found in the curves of all the alcohols down to dodecyl (Fig. 4). A change noticeable to the naked eye took place at this transition; the crystals first forming were transparent but at the transition point the melt became white and amorphous looking. For decyl, undecyl and dodecyl no arrest was found in the curve of the dry alcohol, but cooling the alcohol below zero seemed to introduce some impurity, for the alcohol would not then give a flat cooling curve but supercooled greatly and would show a peak below the original setting point and then come down. Alcohols showing this type of curve would also show a decided transition point. In the light of Garner, Madden and Rushbrooke's experience with acids containing a trace of water and the author's experience with wet uneven acids it seems logical to suppose that water is the impurity introduced by the low temperature. Thus the presence of the transition in the curve for these alcohols can be explained. The transition in the higher alcohols cannot be explained in this manner for they had been distilled. If the heat of this transition is less for lower members of the group, the presence of the water might be necessary to make the change rapid enough to be noticeable. Malkin gives data only on even alcohols; in this work a transition was found not only for the even alcohols: tetradecyl, cetyl and octadecyl, but also for the uneven ones: tridecyl, pentadecyl and heptadecyl.

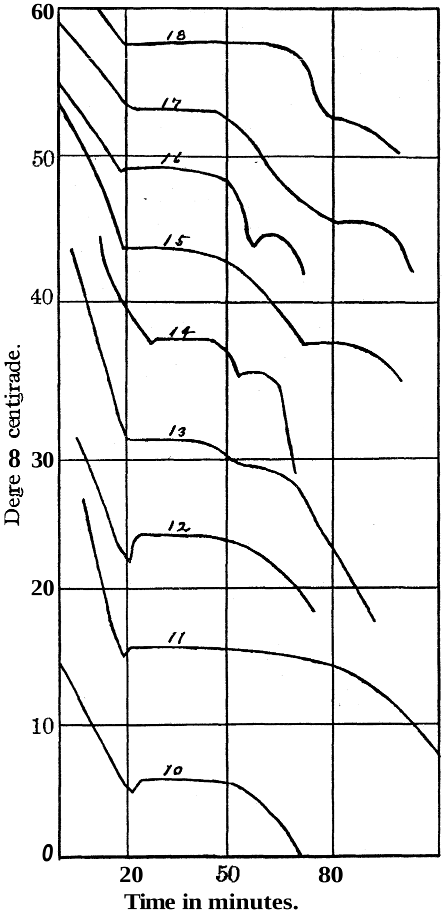


Fig. 4.—Alcohols.

The acetates proved to be the most interesting compounds studied. For cetyl and octadecyl two fusion points were found, while heptadecyl gave only one; but below cetyl it was the uneven acetates which gave two fusion points, while the even acetates displayed only one. Only one parallel occurrence was found: Francis, Piper and Malkin[2] find one crystal spacing shown by the uneven acids up to and including pentadecoic and by the even acids starting with palmitic. In plotting the fusion points of the acetates it seems as though the curve for the beta form of the acetates of uneven alcohols is continued in that of the beta form of the even acetates. And, likewise, the alpha form for the lower uneven acetates seems continued in that of the alpha form for the higher even acetates. The value for heptadecyl acetate lies on the curve for the alpha forms of the even acetates to whose cooling curves its cooling curve is similar. But the fusion points of the lower even acetates which have the same type of curve lie on a curve which is slightly above the curve for the beta form of the uneven acetates.

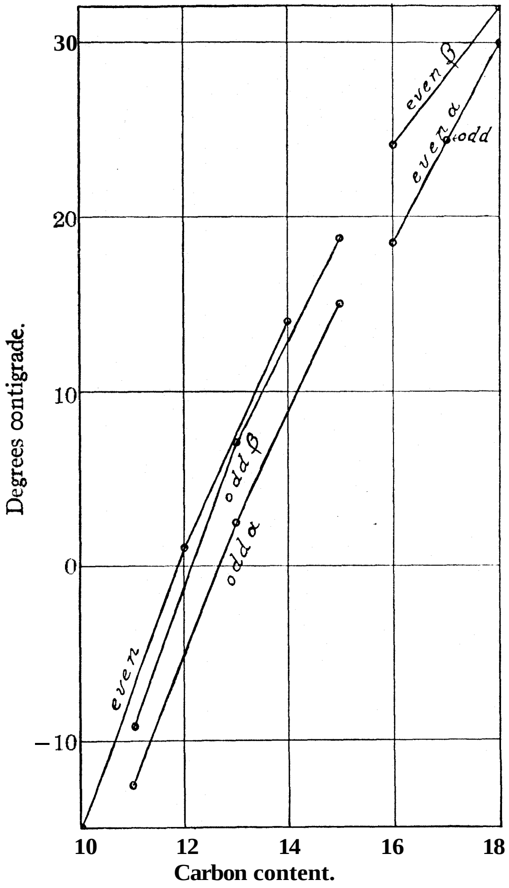
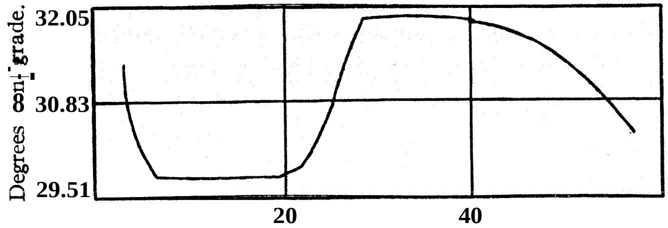


Fig. 5.—Melting points of acetates.

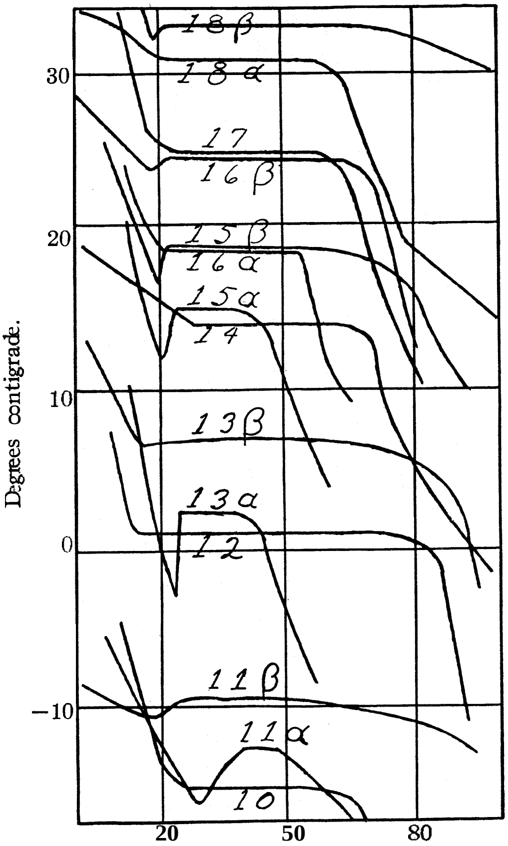
The cooling curves for these acetates are worthy of mention. The acetate cools until the alpha form begins to crystallize. It displays a flat curve until the substance is solid and then cools further, but soon the beta crystal begins to form and the curve will rise to the higher fusion point. If the melt is disturbed even slightly during the formation of the alpha crystals the cooling curve rises to the fusion point of the beta variety (Fig. 6). With the alpha form for octadecyl and cetyl there was no supercooling; likewise with the acetates having only one fusion point—heptadecyl, tetradecyl, dodecyl and decyl. In order to obtain an accurate value for the beta form the melt was seeded with crystals cooled to the temperature of carbon dioxide snow on the end of a heavy sealed capillary, but even with such seeding and with vigorous stirring there was always considerable supercooling with the beta varieties for either even or uneven acetates. Despite this supercooling it was possible to obtain reproducible values. In



Time in minutes.

Fig. 6.—Cooling curve of octadecyl acetate.

the alpha variety of the uneven acetates there was also decided supercooling, but no attempt could be made to prevent this since to disturb the melt would cause the beta crystal to form. In spite of this, reproducible values for the fusion points could be obtained. In this mass of similarities and dissimilarities only an x-ray study can prove conclusively what forms are related, and whether we have to deal here with two forms, alpha and beta as here used, or whether there may be three, four or even more different crystal spacings.



Time in minutes.

Fig. 7.—Acetates.

The ethyl esters combine the two forms of dimorphism which have been found in these compounds by Smith[10] and Phillips and Mumford.[8] Malkin[11] in an x-ray study of ethyl and methyl esters found two forms for the ethyl esters, apparently alpha and gamma forms from his description. For the methyl esters he found that only those of the odd acids showed the two forms.

The crystals of ethyl palmitate and ethyl stearate which are obtained by crystallizing from alcohol are of the higher melting variety. Smith, Phillips and Mumford used these crystals to seed the melt to obtain the fusion point of the beta variety. To obtain a true fusion point they kept the esters at the setting point for a long time until crystallization was finally accomplished. With the exception of these two articles there is no mention in the literature of the lower-melting crystalline form. If melting point measurements were made it would be easy to see why this is so because the crystals of an ester which had been well solidified or had been crystallized from ethyl alcohol would be of the beta variety.

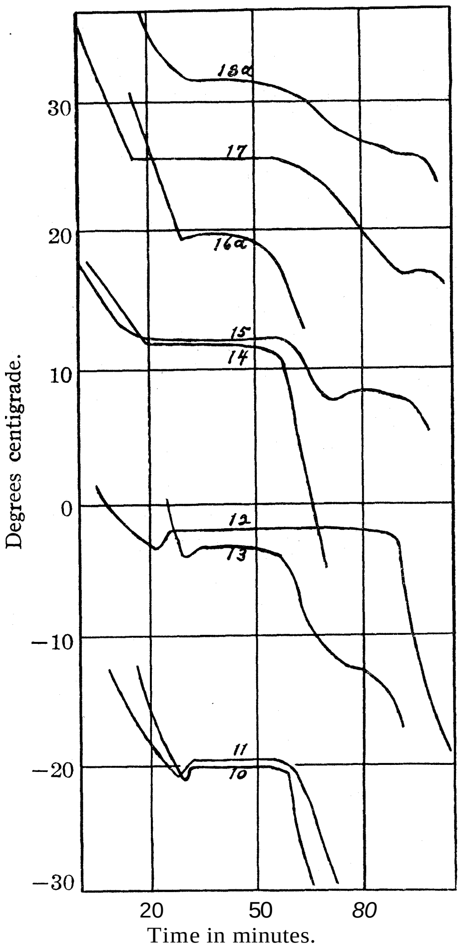


Fig. 8.—Ethyl esters.

In our work great difficulty was encountered in obtaining the setting points of these two ethyl esters. With ethyl stearate it was easy to obtain a cooling curve for the lower melting alpha crystal though the curve obtained began to fall too soon—and then fell too gradually. The lower part of the curve was of no value for the beta crystal began to form and made two successive humps in the curve. Phillips and Mumford also speak of getting a cooling curve for the alpha variety with retardation due to the formation of the beta crystal. The apparatus used by us did not permit keeping the ester at a certain temperature for any length of time so that it was impossible to obtain a fusion point for the beta crystal. With the palmitate it was difficult to get a curve for even the alpha variety because the two crystals grew simultaneously. The lower melting crystal would start to form in long needles in the melt and then small clumps of much smaller compact would begin to grow and cause the temperature to rise. An inferior curve was thus obtained for the lower melting crystal but again it was impossible to obtain a curve for the higher melting variety. Since the higher melting point has been studied by many workers it was thought more valuable for our purposes to obtain a value for the lower one. In the curves for the uneven esters transitions were found in the cooling curves of the solids of ethyl tridecoate, pentadecoate and heptadecoate.

Experimental

Preparation of Materials.—The compounds were prepared from 22.5 kilos of coconut oil which was saponified with 40% sodium hydroxide. To 4 kg. of the liberated acids, 4 liters of 95% alcohol and 825 g. of calcium chloride and hydrogen chloride gas were added and the mixture was heated for thirty-six hours After cooling the aqueous layer was siphoned off and 140 g. of calcium chloride and more hydrogen chloride were added. After twelve more hours of heating the free acid was usually less than 2% The ester layer was well washed with water and then with very dilute ammonia.

The mixture of esters was fractionated at 15 mm. at first through a simple column and then through a precision still of the Peters and Baker[11] type. The portion boiling higher than ethyl myristate was completely hydrogenated at 2 atm. pressure with a nickel catalyst. The fractionation was repeated until cuts were obtained which boiled constantly.

It was found best to convert the ethyl esters into butyl by heating them in excess butyl alcohol containing hydrogen chloride in the pot of a column still until the lower alcohol was eliminated.

The esters were reduced to the corresponding alcohols by a modification of the Beauveault and Blanc method.[12] The charge was 1.5 moles of the ester, 3 liters of butyl alcohol and 180 g. of sodium. When the reaction was over 160 cc of water was added cautiously and the mixture heated for an hour to ensure saponification of any ester present. The mixture was cooled to 80° and 1200 cc. more water added. After agitation the butyl alcohol layer was separated and washed with two 500-cc. portions of 20% brine. To this was added a concentrated water solution of 40 g. of calcium chloride The butyl alcohol was driven off by steam distillation and the hot mixture of alcohol and calcium soap poured into a large dish. The alcohol was extracted from the calcium soap with toluene, larger amounts being required for the higher alcohols. The yields of the alcohols were from 81 to 87%.

The bromides were prepared by passing gaseous hydrobromic acid into the alcohol kept at 140–150° or at 130" for the lower boiling alcohols. The water formed was carried over by the excess of the acid which was caught in a cold water trap along with some of the alcohol and bromide that were carried over; when no more water seemed to be evolved the alcohol–bromide mixture was cooled, poured into a pressure bottle and saturated with hydrogen bromide in the cold or at its melting point. The bottle was closed and heated for an hour at 150°. It is important to push the conversion as far as possible since if much of the alcohol is left emulsions are formed. The crude bromide was washed with sodium sulfate solution and then with concd. sulfuric acid as long as anything was removed, and again with the sodium sulfate solution. The yields were 84 to 96%. The bromides were further purified by fractionation. This method is an adaptation of that used by Moslinger,[13] Guthzeit,[14] Krafft[15] and Adams and Dyer[16] for iodides; and by Ruzicka, Stall and Schinz,[17] and Oskerko[18] for bromides.

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(11) Peters and Baker, *Ind. Eng. Chem.*, 18, 69 (1926).

(12) Beauveault and Blanc, *Compt. rend.*, 136, 1676 (1903); 137, 60 (1903).

(13) Moslinger, *Ann.*, 185, 49 (1877).

(14) Guthzeit, *ibid.*, 206, 351–367 (1881).

(15) Krafft, *Ber.*, 19, 2984 (1886).

(16) Adams and Dyer, *J. Chem. Soc.*, 127, 70–73 (1925).

(17) Ruzicka, Stall and Schinz, *Helv. Chim. Acta*, 11, 670–686 (1928).

(18) Oskerko, *J. Russ. Phys.-Chem. Soc.*, 46, 411–416 (1914).

The acetates were prepared by the usual method of heating the alcohol with acetanhydride and fused sodium acetate.

The uneven acids were obtained through the nitriles which were prepared by the method of Adams and Marvel,[19] heating seventy-two hours to complete the reaction. The purified nitrile was saponified by heating for twelve hours in butyl alcohol and sodium hydroxide. The butyl alcohol solution was washed with water to remove the excess alkali and treated with calcium chloride. The calcium soap was freed from butyl alcohol by steam distillation and from water by filtration, dried and then washed with toluene until it became fluffy and white. The acids were set free, well washed with hot water and converted into their ethyl esters which were then fractionated in the precision still. The yield from the bromides to the acids were 85–90%.

Apparatus

The time–temperature curves were made by the use of a copper–constantan thermocouple according to the method of Andrews, Kohman and Johnston.[20] The container for the melt was an adaptation of that described by Southard and Andrews.[21] A type K potentiometer and sensitive galvanometer were used to measure the e. m. f. Temperatures below zero centigrade were determined from the scale of Southard and Andrew~.~'For temperatures above 0°C. a scale contained in an unpublished part of the dissertation of R. H. Smith of this University was used. The thermocouples were carefully calibrated. The fusion points were checked and rechecked; an accuracy of one microvolt was obtained, which is in the neighborhood of 0.02".

Summary

The normal primary alcohols from decyl to octadecyl, their acetates and the corresponding bromides and also the acids and their ethyl esters have been prepared and purified with care.

The setting points have been determined accurately. The melting points of the alcohols do not show detectable alternation but the bromides do. Many of the acetates and ethyl esters show dimorphism.

BALTIMORE. MARYLAND

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(19) Adams and Marvel, THIS JOURNAL, **42**, 299 (1920).

(20) Andrews, Kohman and Johnston, *J. Phys. Chem.*, 49, 914 (1925).

(21) Southard and Andrews, *J. Franklin Inst.*, 407, 3, 323–339 (1929).

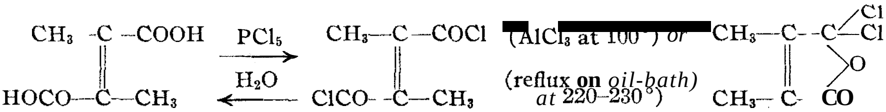
[CONTRIBUTION NO. 107 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies on Unsaturated 1,4-Dicarbonyl Compounds. VIII. Some New Derivatives of Dimethylfumaric Acid

BY ROBERT E. LUTZ AND ROBERT J. TAYLOR[*]

The substitution of two methyl groups in fumaric and maleic acids markedly alters the ease and in some cases the direction of rearrangement; for instance, maleic and citraconic acids with catalysts are rearranged into the trans isomers, but dimethylfumaric acid goes readily to dimethylmaleic anhydride under analogous conditions.[1] This paper deals with some related studies which were made preliminary to the synthesis of aryl dimethyl unsaturated 1,4-diketones and ketonic acids.[2]

Dimethylfumaryl Chloride (II).—Dimethylfumaric acid (I) forms a normal di-acid chloride (II) which is hydrolyzed rapidly and quantitatively back to the trans acid, reacts with methanol to give the diester (V) and with aniline to give the dianilide, and undergoes the Friedel and Crafts reaction to give diketones.[2] When it is heated with aluminum chloride at 100° it is rearranged completely into the cis acid chloride (III) which is known.[3] Heating without catalyst at boiling temperature also brings about this rearrangement, although considerable decomposition occurs as well.



I II III

The inversion of the trans acid chloride to the *cis* may be regarded as evidence that the latter has the dichlorocrotolactone structure (III), since this formulation would account for the rearrangement in terms of cyclization as the driving force. The energy change in inversion of the configuration alone, without other change in the molecule, would be expected to be very small but negative, and should lead if anything to rearrangement in the opposite direction (from cis to trans) as it does in the various inversions of maleic and citraconic acids and the unsaturated 1,4-diketones and ketonic esters. The easy rearrangement of dimethylfumaric acid to dimethylmaleic anhydride is obviously due to the formation of a stable ring as the driving force,[1a] and is therefore analogous.

The cis acid chloride[4] in contrast with the trans isomer reacts relatively

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[*] Du Pont de Nemours Fellow, 1931–1932.

(1) *Cf.* (a) Fittig, *Ber.*, 29, 1842 (1896); (b) Fittig and Kettner, *Ann.*, 304, 156 (1898); (c) Ott, *Ber.*, 61, 2124 (1928).

(2) Lutz and Taylor, THIS JOURNAL, **55**, 1593 (1933).

(3) (a) Otto and Holst, *J. prakt. Chem.*, [2] 42, 72 (1890). Cf. the rearrangement of dibromofumaryl chloride; (b) Ott, *Ann.*, **392**, 270 (1912).

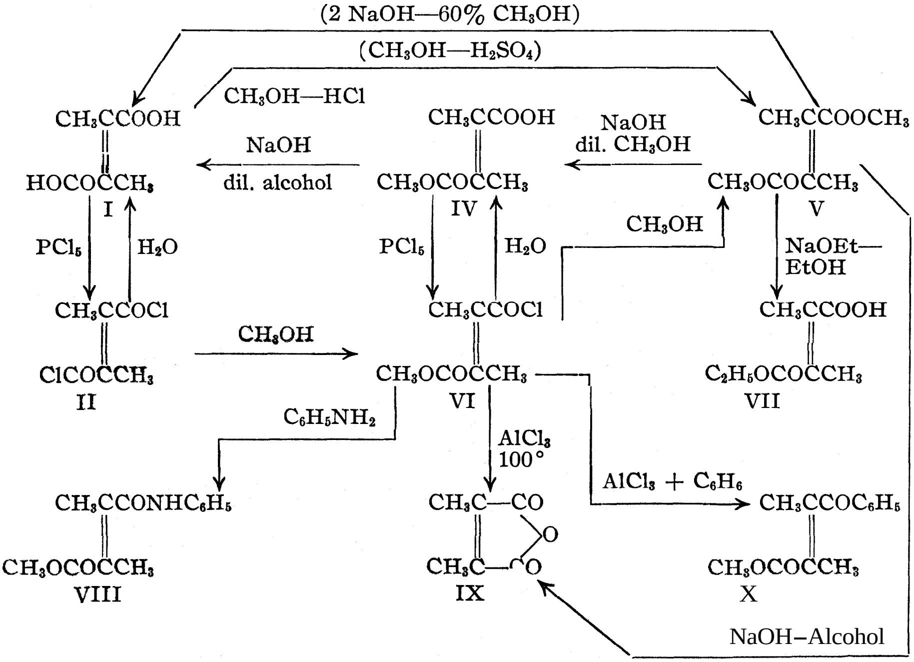
(4) *Cf.* also citraconyl chloride; Lutz and Taylor. THIS JOURNAL, 56, 1168 (1933).

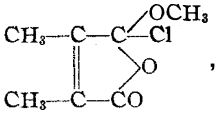
very slowly with water, a phenomenon which might possibly be accounted for on the basis of the cyclic formulation (III).

The Monoalkyl Acid Esters and Ester Chlorides.—The monomethyl acid ester (IV) is best obtained by the partial hydrolysis of the dimethyl ester (V) in dilute methanol with alkali, but when this reaction is carried out in ethanol–ether mixtures, displacement of methyl occurs and the mono-ethyl acid ester (VII) is obtained in good yield. The acid methyl ester may be prepared also, though in poorer yields, by partial esterification of the acid (I).

The monoalkyl ester acid chlorides (VI) are readily prepared from the acid esters by the action of phosphorus pentachloride, but are obtained in only very small yield by partial alcoholysis of the di-acid chloride. They are easily hydrolyzed back to the corresponding alkyl acid esters, are alcoholized to the diesters (V), react with aniline to give mono-anilides (VIII), and undergo the Friedel and Crafts reaction to give *trans*-aroyldimethylacrylic esters (X).[2]

The monomethyl ester mono-acid chloride (VI) is converted into dimethylmaleic anhydride with the loss of methyl chloride by heating with an excess of aluminum chloride at 100°. This reaction is analogous with the rearrangement of dimethylfumaryl chloride to the cis isomer, and with the dehydration of dimethylfumaric acid to the cis anhydride. The formation of the hypothetical *cis*-(ψ)-dimethylmaleic monomethyl ester mono-

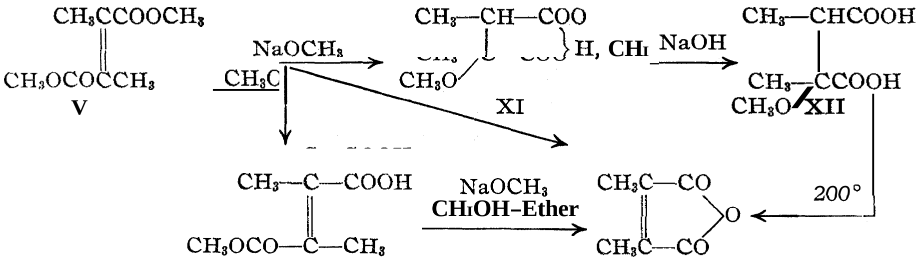


acid chloride, , as an intermediate in the reaction, is possible.

Addition and Inversion.—Auwers[5] found that the hydrolysis of dimethylfumaric dimethyl ester with alcoholic alkali at room temperature gives regularly dimethylmaleic anhydride, but Curtius and Müller[6] using aqueous sodium hydroxide got normal hydrolysis without inversion of the configuration.

In the course of a number of experiments we have found also that both of the diesters and the monomethyl acid ester undergo rearrangement during hydrolysis in alcohol in which the water content is minimized; but invariably in dilute alcohol containing as much as 40% of water, nearly quantitative yields of dimethylfumaric acid are obtained with no detectable amounts of inversion or addition products. These rearrangements must occur during hydrolysis and not subsequently, since dimethylfumaric acid itself is stable under these conditions.

In the partial hydrolysis of dimethylfumaric dimethyl ester using one equivalent of sodium methylate in a methanol–ether mixture, the main product proved to be dimethylmethoxysuccinic monomethyl ester (XI), a compound formed obviously by the 1,4-addition of sodium methylate to the unsaturated system[7] with simultaneous hydrolysis of one of the two carbomethoxyl groups. The structure of the addition compound, except for the position of the methoxyl relative to the free carboxyl, was shown by hydrolysis to dimethylmethoxysuccinic acid (XII) and by subsequent pyrolysis to give dimethylmaleic anhydride. Small but significant amounts of dimethylmaleic anhydride and dimethylfumaric monomethyl acid ester (IV) were obtained as by-products of this reaction, but no dimethylfumaric acid.



In these hydrolytic reactions the reagent responsible for inversion, replacement of methyl by ethyl, and addition, must be sodium alcoholate

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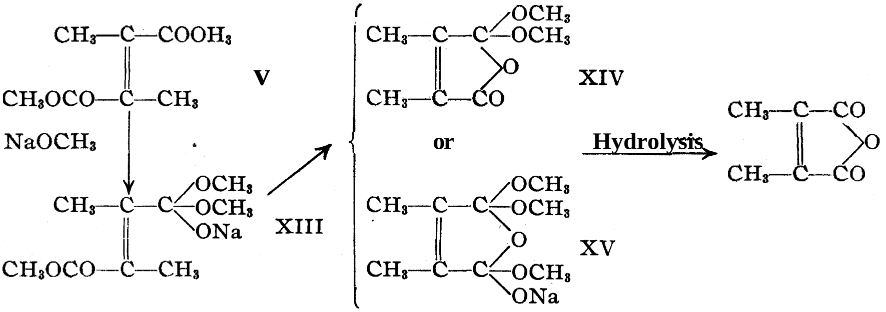
(5) Auwers, *Ber.*, 62, 1678 (1929).

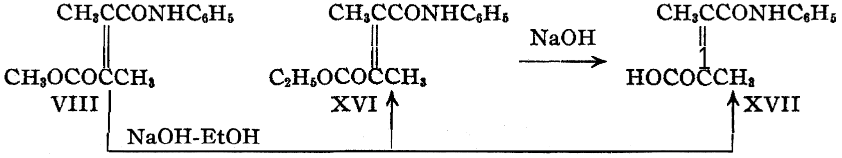
(6) Curtius and Müller, *ibid.*, **37**, 1272 (1904).

(7) Dimethyl fumarate undergoes this reaction readily in the presence of a trace of sodium methylate. (a) Perdue and Marshall, *J. Chem. Soc.*, 59,468 (1891). Cf. also (b) Claisen and Crismer, *Ann.*, **218**, 143 (1883); (c) Liebermann, *Ber.*, *26*, 1876 (1893); Hinrichsen, *Ann.*, *336*, 202 (1904); etc.

(rather than sodium hydroxide) because these reactions occur only in alcohol or alcohol–ether mixtures in which the effective alcoholate concentration is relatively high. Furthermore, a carbomethoxyl group is involved because dimethylfumaric acid in which this group is absent is stable under similar conditions. It seems unlikely that inversion of the configuration in the hydrolytic reactions involves actual addition of methanol to the ethylene linkage because such addition compounds are known and do not decompose easily. It is of course possible that of the two theoretically possible diastereoisomeric addition compounds, one might decompose much more easily than the other to lose the addenda and thus lead to inversion; or that an intermediate 1,4-addition product might be so unstable as to decompose similarly rather than undergo rearrangement into a stable dimethylsuccinic acid derivative. We are led to suggest another possible mechanism involving the addition of sodium methylate to a carbonyl group, followed by cyclization as the driving force in rearrangement, in which case possibly the cis di- or mono-alkyl esters are intermediates if the cyclic dihydroxylactone formulas suggested by Anschütz[8] are correct. In the illustration below inversion is shown as preceding hydrolysis, although partial hydrolysis might equally well take place first.



The Anilides.—Dimethylfumaryl chloride and the monomethyl and ethyl ester mono-acid chlorides react immediately in ether solution with aniline to give in each case the corresponding anilides. The two monoalkyl ester monoanilides both undergo partial hydrolysis in ethanolic alkali to the same monoanilide of dimethylfumaric acid (XVII). In the case of the monomethyl ester monoanilide (VII), curiously, although an excess of alkali was used, hydrolysis went only part way, but the methyl



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[8] Anschütz, *Ann.*, **254**, 168 (1889); 461, 155 (1928). See also Ref. 6.

group was replaced by ethyl in the unhydrolyzed material. The dianilide was slowly hydrolyzed when boiled with alcoholic alkali, yielding, however, dimethylmaleic anhydride.

Experimental Part

Dimethylfumaric acid was prepared according to Ott.[1c] A few typical runs on the inversion of dimethylmaleic anhydride are summarized in the table.

No. of runs	Temp., °C.	Time of heating, hrs.	% Yields of A	B	C
5	180	45–48	50–60	2339	9–12
3	180	64–72	32–44	38–43	11–14
4[a]	189–190	44-64	27–40	41–46	13–18

A, Dimethylmaleic anhydride; B, dimethylfumaric acid; C, methyl itaconic acid

[a] Two of these runs started with methyl itaconic acid.

At 180°, sixty-five to seventy hours is required to establish equilibrium and a somewhat shorter time, forty-five hours, at 190°.

0.2 g. of the acid was allowed to stand for forty-one hours in 7 cc of absolute methanol and 2.7 cc. of absolute ether containing 0.1 g. of dissolved sodium; 0.15 g. of the acid was recovered and identified, and no trace of dimethylmaleic anhydride was detected.

Dimethylfumaric dimethyl ester (V)[5] was prepared by adding 50 g. of dimethylfumaryl chloride dropwise with stirring to 25 cc. of absolute methanol over a period of one hour. A nearly quantitative yield of the ester crystallized on cooling (47.3 g).

One gram of the dimethyl ester was allowed to stand overnight in 15 cc. of 60% methanolic sodium hydroxide (2 equiv.). The solution was then further diluted with water and extracted with ether. The aqueous solution of the sodium salts was then acidified, and the product isolated by extracting with ether; yield 0.78 g. (93%) of nearly pure dimethylfumaric acid.

Dimethylfumaryl Chloride (II).—Dimethylfumaric acid (168 g.) was allowed to react with 486 g. of phosphorus pentachloride. The mixture of acid chloride and phosphorus oxychloride was separated by two fractional distillations at 20 mm. using a 61-cm. Vigreux column; 193 g. of dimethylfumaryl chloride was obtained (91.5%) (together with an end fraction of 2.7 g. of dimethylmaleic anhydride; (b. p. 100–105' at 8 mm.)). The acid chloride is a nearly colorless oil; b. p. 79.5" at 22 mm.

Anal. Calcd. for $C_6H_6O_2Cl_2$: C, 39.79; H, 3.34. Found: C, 39.58; H, 3.24.

A sample of the acid chloride was hydrolyzed with water, on standing for twenty-four hours or shaking for one to two hours, to give the acid in quantitative yield.

Dimethylfumaric dianilide, $C_6H_5NHCOC(CH_3)=C(CH_3)CONHC_6H_5$, was prepared by adding the di-acid chloride to an absolute ether solution of 4 equiv. of aniline; yield from 0.95 g. of acid chloride was 1.8 g.; cryst. as twinned rectangular prisms from ethanol; m. p. 267" (corr.).

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.47; H, 6.17. Found: C, 73.55; H, 6.17.

A small sample was boiled in dilute alcoholic sodium hydroxide for five hours. It was diluted with water and extracted with ether, from which, by extracting with hydrochloric acid, a solution of aniline was obtained which gave a characteristic precipitate with bromine. The aqueous solution of sodium salts was acidified and extracted with ether, from which dimethylmaleic anhydride was recovered by steam distillation.

Rearrangement of Dimethylfumaryl Chloride.—Two grams of the acid chloride was heated with 3.7 g. of anhydrous aluminum chloride at 100° for two and one-half hours. The mixture was hydrolyzed by allowing it to stand in water overnight. The products were extracted with ether. Steam distillation of the solid residue gave 0.65 g. of dimethylmaleic anhydride (47%). From the aqueous residue 0.1 g. of dimethylfumaric acid was recovered. The crude mixture containing the cis acid chloride was only partly hydrolyzed when shaken violently (machine) with water for four hours.

In a similar experiment a sample of dimethylfumaryl chloride was refluxed on an oil-bath (200–230°) for one and three-tenths hours. Some decomposition occurred, and a considerable yield of dimethylmaleic anhydride was isolated upon hydrolysis.

The Acid Esters of Dimethylfumaric Acid.—In the partial hydrolysis of the diester and the partial esterification of the acid, a convenient method of separating mixtures of the di-acid, monomethyl acid ester, and dimethyl ester, was followed; ether extraction of an alkaline solution removed the diester; acidification and a second ether extraction removed the acidic constituents which were isolated upon evaporation of the solvent; the acid ester was extracted from the insoluble dimethylfumaric acid by means of boiling ligroin from which it crystallized on cooling.

In the esterification of dimethylfumaric acid the two alpha methyl groups lower appreciably the rate of esterification, as was shown by comparing the low yields of acid ester and dimethyl ester from esterification in boiling 4% methanolic hydrogen chloride, with the better yields of the corresponding mesaconic acid derivatives obtained by Anschütz under similar conditions.[9]

Dimethylfumaric Monomethyl Acid Ester (IV).—The dimethyl ester (33.5 g.) was dissolved in 200 cc. of 95% methanol containing 11.2 g. of potassium hydroxide and allowed to stand for twenty hours. The mixture was diluted with water and the products separated as described above; yields, 5.5 g. (16.5%) of dimethyl ester, 17.5 g. (61%) of monomethyl ester, and 0.5 g. (2%) of dimethylfumaric acid; cryst. as needles from ligroin in which it is moderately soluble hot; m. p 81° (corr.).

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.14; H, 6.38. Found: C, 53.13; H, 6.30.

A small sample of the monomethyl ester was treated with a slight excess of 2 equivalents of sodium dissolved in 2 5 parts of absolute alcohol and 0.8 part of *dry* ether, and allowed to stand for forty-one hours. An oily product (acidic) was obtained, from which a small yield of dimethylmaleic anhydride was isolated and identified. Hydrolysis in dilute alcohol gave dimethylfumaric acid in good yield.

Partial Esterification of Dimethylfumaric Acid.—A solution of 25 g. of dimethylfumaric acid in 100 g. of 4% absolute methanolic hydrogen chloride was refluxed for one hour, and was then decomposed in ice and sodium carbonate, and the products extracted and separated as described above; yields, 0.75 g (2%) of the dimethyl ester, 3.4 g. (15%) of acid ester, and 11.6 g. (46%) of unchanged acid.

In another experiment 25 g. of the acid was allowed to stand for eighteen hours in saturated methanolic hydrogen chloride solution; yields, 6.5 g. (22%) of dimethyl ester, 8.89 g. (32%) of acid ester, and 4.5 g. (18%) of unchanged acid.

Partial alcoholysis of dimethylfumaryl chloride in benzene with one equivalent of methanol gave a mixture of products which consisted largely of diester and unchanged material and a small amount of mono-acid chloride monomethyl ester. The mixture was not easily separated and the mono-acid chloride was not isolated, but it was shown to be present by a Friedel and Crafts reaction on the mixtures, which gave small yields of trans-benzoyldimethylacrylic acid and dimethylfumaric monomethyl acid ester, both of which were derived from the mono-acid chloride.

Dimethylfumaric Monomethyl Ester Mono-acid Chloride (VI).—The acid ester (22.7 g.) and 31 g. of phosphorus pentachloride reacted to give a liquid mixture which was fractionally distilled at 20 mm.; yield of pure acid chloride, 20 g. (79%); colorless oil; b. p. 90–91° (corr.) at 20 mm.

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[9] Anschütz, *Ann.*, 363, 139 (1907).

Anal. Calcd. for $C_7H_9O_3Cl$: C, 47.58; H, 5.14. Found: C, 47.14, 47.06; H, 5.89, 5.04.

One gram of the acid chloride was added to methanol; 0.72 g. of the dimethyl ester crystallized on cooling.

One gram reacted in less than two hours with water, from which on cooling 0.85 g. (95%) of monomethyl acid ester was isolated

One-half gram of the acid chloride was heated at 100° with 2 g. of aluminum chloride for three hours. Gas evolution took place. The mixture was hydrolyzed and extracted with ether, which on evaporation and steam distillation gave 0.16 g. (32%) of dimethylmaleic anhydride.

Dimethylfumaric Monomethyl Ester Monoanilide (VIII).—Prepared by the action of the monomethyl ester monochloride on aniline in dry ether; cryst. slowly as microscopic scales from benzene and ligroin (requires careful seeding); m. p. 74–75" (corr.).

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.91; H, 6.44. Found: C, 66.79; H, 6.45.

Dimethylfumaric Acid Monoanilide (XVII).—The above monomethyl ester monoanilide (0.6 g.) was hydrolyzed with the calculated amount (1 equiv.) of sodium hydroxide in 5 cc. of 85% ethanol (forty-one hours standing) and gave an alkali-insoluble fraction (0.22 g. 36%) of m. p. 119–120°, identified as the corresponding monoethyl ester monoanilide. The hydrolyzed portion (alkali soluble), 0.36 g., (61%) crystallized from ether and ligroin; m. p. 195" (corr.).

Anal. Calcd. for $C_{12}H_{13}O_3N$: C, 65.76; H, 5.98. Found: C, 65.95; H, 6.04.

Dimethylfumaric Monoethyl Acid Ester (VII).—Dimethylfumaric dimethyl ester (47.3 g.) was treated with a solution of 6.6 g. of sodium in 350 cc. of 95% ethanol and 120 cc. of ether. The solution was allowed to stand for twenty-four hours and was then diluted with water and the ether layer separated, from which an oily di-ester (4.3 g.) was recovered and identified by hydrolysis to dimethylfumaric acid. The aqueous solution of the sodium salts was acidified and extracted with ether. After drying over sodium sulfate, the ether was evaporated and the oily residue distilled at 5 mm.; 2.3 g. (b. p. 84–86°) of dimethylmaleic anhydride, and 29.1 g. (b. p. 124–129°) (61.5%) of monoethyl ester of dimethylfumaric acid, were isolated and identified; 1.8 g. of dimethylfumaric acid was recovered from the residue in the distilling flask. The monoethyl ester is a colorless oil of b p. 118° at 1 mm.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.78; H, 7.03. Found: C, 54.75, 54.85; H, 6.94, 6.89.

A sample was hydrolyzed on standing for thirty-six hours in a 10% solution of sodium carbonate, in which it dissolved easily with evolution of carbon dioxide. The mixture was distilled, and the ethyl alcohol liberated was converted into iodoform and identified by a mixed melting point. **A** test for methanol was negative.

One gram of the monoethyl ester was hydrolyzed by standing overnight in 10 cc. of a solution of one equivalent of sodium hydroxide in 50% ethanol; 0.83 g. of nearly pure dimethylfumaric acid was recovered and identified.

Dimethylfumaric Monoethyl Ester Mono-acid Chloride, $C_2H_5OCOC(CH_3)=C(CH_3)COCl$.—The monoethyl ester (21 g.) was allowed to react directly with one equivalent of phosphorus pentachloride. The resulting liquid products were fractionally distilled at 15 mm. using a 38-cm. Vigreux column; yield 20.7 g. (89%) of nearly pure acid chloride; colorless oil, b. p. 90–91° at 14 mm.

Anal. Calcd, for $C_8H_{11}O_3Cl$: C, 50.38; H, 5.82. Found: C, 49.93, 50.04; H, 5.72, 5.39.

Upon hydrolysis in 60% alcoholic potassium hydroxide, a nearly quantitative yield of dimethylfumaric acid was recovered and identified.

Dimethylfumaric Monoethyl Ester Monoanilide (**XVI**).—Prepared from the monoethyl ester monochloride with aniline in dry ether; yield 0.7 g. from 0.6 g. of acid chloride; cryst. as thin rectangular scales from benzene and ligroin, m. p. 121.5–122° (corr.).

Anal. Calcd. for $C_{14}H_{17}O_3N$: C, 68.00; H, 6.94. Found: C, 68.10; H, 6.90.

Hydrolysis of 0.1 g. with 1 equiv. of sodium in 2 cc. of 85% ethanol (forty-one hours standing) gave 0.08 g. of unchanged material and 0.015 g. of dimethylfumaric acid monoanilide which was identified.

1,2-Dimethylmethoxysuccinic Monomethyl Acid Ester (XI).—Dimethylfumaric dimethyl ester (37 g.) was allowed to stand for thirty-eight hours in a mixture of 250 cc. of absolute methanol and 100 cc. of commercial anhydrous ether, containing 5.3 g. of dissolved sodium. The solution was diluted with water and extracted with ether, from which 6.3 g. of a colorless oil was obtained on distillation at 2 mm. pressure (b. p. 70–80°). By oversight this oil was not investigated. It probably contained unchanged dimethylfumaric dimethyl ester and dimethylmethoxysuccinic dimethyl ester. The aqueous solution of sodium salts was acidified and extracted with ether and the products distilled at 2 mm.; the first fraction, b. p. 75–80", solidified and was identified after recrystallization as dimethylmaleic anhydride. More was isolated from the second and third fractions, which consisted largely of dimethylfumaric monomethyl ester. The separation was made by extracting the mixture with dilute sodium carbonate solution and filtering quickly before the dimethylmaleic anhydride dissolved. The monomethyl ester was recovered from the filtrate. The fourth fraction proved to be nearly pure dimethylmethoxysuccinic monomethyl ester; colorless oil; b. p. 130–131° at 2 mm.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.50; H, 7.42. Found: C, 50.79; H, 7.26.

1,2-Dimethylmethoxysuccinic Acid (**XII**).—The monomethyl ester (1 g.) was dissolved in 10 cc. of 60% alcoholic sodium hydroxide (one equiv.) and allowed to stand for twenty hours. The mixture was diluted with water, washed with ether, and the aqueous layer acidified and extracted with ether, from which an oil was isolated on subsequent evaporation. The oil, taken up in benzene, deposited 0.2 g. of crystals; cryst. from benzene, m. p. 133.5" (corr.).

Anal. Calcd. for $C_7H_{12}O_5$: C, 47.70; H, 6.87. Found: C, 47.86; H, 6.88.

Pyrolysis.—The acid (0.04 g.) was heated to 200° in a small test-tube immersed in an oil-bath. On cooling, 4 drops of water was added and the mixture distilled. A small amount of dimethylmaleic anhydride solidified in the delivery tube and was identified by a mixed melting point.

Summary

A number of new derivatives of dimethylfumaric acid and its monomethyl and ethyl acid esters are described. Rearrangement of the *trans* configuration to the cis, addition, and replacement of methyl by ethyl, under the influence of alkali, are discussed.

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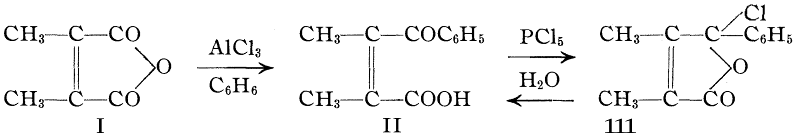
Studies on Unsaturated 1,4-Dicarbonyl Compounds. IX. Aryl Unsaturated 1,4-Diketones and Ketonic Acids Derived from Dimethyl Maleic and Fumaric Acids

BY ROBERT E. LUTZ AND ROBERT J. TAYLOR*

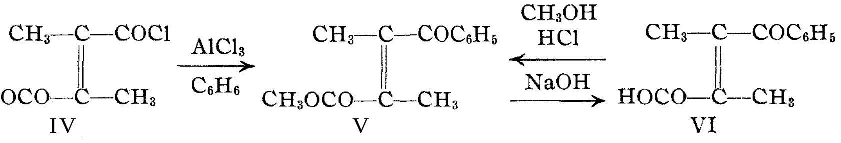
This paper deals with the synthesis and preliminary study of a new series of compounds which should yield diastereoisomeric reduction products. A study of the stereochemistry of reduction is in progress in this Laboratory and will be treated in a later paper.

Cis-β-benzoyldimethylacrylic Acid (II).—The Friedel and Crafts reaction on dimethylmaleic anhydride gives cis-benzoyldimethylacrylic acid (II) in good yield as the sole product. The configuration must be *cis* corresponding with that of the starting material, because the isomer (obviously the trans) is obtained exclusively in a synthesis from dimethylfumaric acid, and because the acid chloride (III) does not give any detectable amount of a diketone in the Friedel and Crafts reaction, in contrast with the trans isomer which behaves normally in this respect.



The methyl ester is easily made and is hydrolyzed to the acid again in good yield. It is quite stable in solution toward iodine and sunlight, and cannot be prepared from the trans isomer by the action of sunlight alone. The configurations of these dimethyl compounds, then, are relatively stable as compared with those of the unsubstituted aroyl acrylic esters.

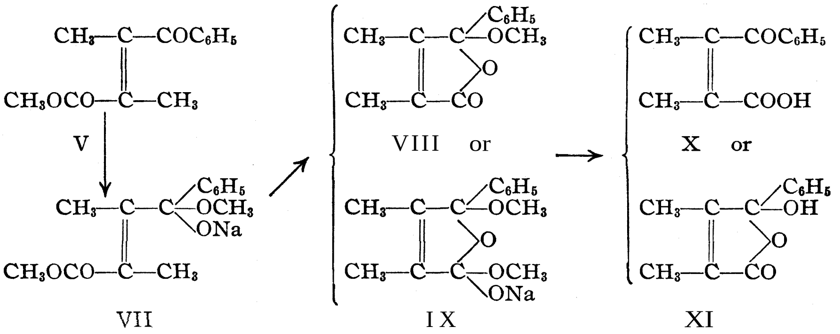
Trans-β-benzoyldimethylacrylic Acid (VI).—*Trans*-benzoyldimethylacrylic methyl and ethyl esters (V) were obtained as the sole products of the Friedel and Crafts reaction on the corresponding acid chlorides of dimethylfumaric monoalkyl acid esters (IV). Hydrolysis of these esters in dilute alcohol gives the corresponding trans acid exclusively, no trace of the *cis* isomer being found. The trans acid is easily esterified, and gives a normal acid chloride (XVII) which undergoes the Friedel and Crafts reaction to give the expected diketone (XV), although in poor yield. The trans configuration follows from these relationships.



$$\begin{array}{c} CH_3-C-COCl \\ \| \\ CH_3OCO-C-CH_3 \\ \mathrm{IV} \end{array} \xrightarrow[C_6H_6]{AlCl_3} \begin{array}{c} CH_3-C-COC_6H_5 \\ \| \\ CH_3OCO-C-CH_3 \\ \mathrm{V} \end{array} \underset{\xrightarrow{NaOH}}{\xleftarrow{CH_3OH\ HCl}} \begin{array}{c} CH_3-C-COC_6H_5 \\ \| \\ HOCO-C-CH_3 \\ \mathrm{VI} \end{array}$$

(*) Du Pont de Nemours Fellow, 1931–1932.

Inversion from Trans to Cis.—*Trans*-benzoyldimethylacrylic methyl ester is hydrolyzed with sodium methylate in methanol, to give exclusively the *cis* acid, although in poor yield. This inversion is analogous with that of dimethylfumaric dimethyl ester during hydrolysis under similar condition~. The change apparently takes place during or preceding hydrolysis because the *trans* acid, once formed, is stable under these conditions. The 1,4-addition of sodium methylate might occur as an intermediate step; but compounds resulting from such additions are known[2] and do not lose methanol easily except at elevated temperature. Another possible mechanism, as outlined in the following diagram, involves the addition of sodium methylate to one or both of the carbonyl groups, followed by cyclization (the driving force causing inversion) and hydrolysis; this would explain the direction of rearrangement, which is opposite that which might be expected on the basis of the generaily greater stability of *trans* forms.



The γ-hydroxy crotolactone formulas (VIII, IX, XI) are analogous with the Anschiitz formulas for maleic acid and ester types,[3] and the cyclic formulation of maleil and *cis* aroyl acrylyl chlorides[4] and the various lactonic forms of some substituted aroyl acrylic acids and esters.[4d] A choice between the two formulations of *cis*-benzoyldimethylacrylic acid might possibly be made in favor of the cyclic type (XI) on the basis of the slow rate of solution of the acid in cold sodium bicarbonate, as contrasted with the rapidity with which the *trans* isomer dissolves under these conditions.

β-(2,4,6-Trimethylbenzoyl)-dimethylacrylic Acid. XII.—A trimethylbenzoyldimethylacrylic acid (XII) is obtained in good yield in the Friedel and Crafts reaction on dimethylmaleic anhydride, but this same acid is also obtained by hydrolysis of the methyl ester which was made similarly from dimethylfumaric monomethyl ester mono-acid chloride (IV). Both

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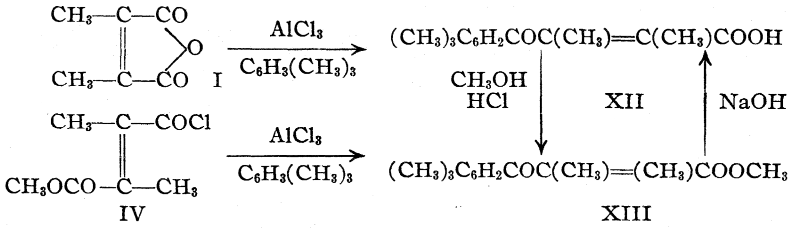
(1) (a) Auwers, *Ber.*, 62, 1678 (1929); (b) Lutz and Taylor, THIS JOURNAL, **55**, in press (1933).

(2) 1. *e.*, 1,2-dibenzoylmethoxyethane; Lutz, THIS JOURNAL, 61,3008 (1929); dimethylmethoxysuccinic acid (Ref. lb), *cf.* discussion (Ref. lb).

(3) Anschiitz, *Ann.*, 264, 168 (1889); 461, 155 (1928). *See* also Ref. la.

(4) (a) Lutz, THIS JOURNAL, **52**, 3405 (1930); (b) Lutz and Taylor, *ibid*, **55**, 1168 (1933); (c) Ott, *Ann*, **392**, 270 (1912); (d) Allen and Frame, *Canadian J. Research*, 6, 605 (1932).

acid and ester must correspond in configuration since they can be converted one into the other by hydrolysis and esterification, involving conditions under which inversion is unlikely.



Obviously in one of these two Friedel and Crafts reactions rearrangement has occurred; there is ample analogy for supposing an inversion from cis to trans in the reaction between citraconic anhydride and mesitylene,[1] and in all of the Friedel and Crafts reactions on maleic anhydride itself;[5] on the other hand, there is no such analogy for the reverse rearrangement from trans to cis. The configuration of this trimethylbenzoyldimethylacrylic acid, then, is very probably trans. A study of the acid chloride failed to yield pertinent information.

The Dimethyl Unsaturated 1,4-Diketones (XV).—The trans aryl unsaturated 1,4-diketones are prepared in good yield by the Friedel and Crafts reaction on dimethylfumaryl chloride (XIV). The dibenzoyl derivative is obtained also, though in poor yield, from *trans*-benzoyldimethylacrylyl chloride (XVII). The preparation of the cis isomers (XVI), however, proved extremely difficult, and was not accomplished in the case of the dibenzoyl derivative. Curiously the *trans*-di-trimethylbenzoyl derivative, the most difficult to isomerize in the unsubstituted series,[6] was partially isomerized in very poor yield by the action of sunlight on a benzene solution. The structure of this cis isomer was shown by reduction to the same products obtained from the trans isomer. It proved to be stable, however, and did not rearrange back to the trans isomer under the influence of iodine and sunlight. It is decomposed when treated with aluminum chloride in carbon disulfide, whereas the trans isomer is stable under these conditions. The configuration of the trans isomer is clear from its synthesis, and that of the cis isomer from its mode of formation from the trans by the action of sunlight.

The 1,6-Addition of Hydrogen to the Dimethyl Unsaturated 1,4-Diketones.—The dimethyl unsaturated 1,4-diketones are reduced easily with zinc and acetic acid to give mainly the furan (XIX). One of the two theoretically possible stereoisomeric saturated 1,4-diketones (XVIII) was isolated also in the case of the reduction of the di-trimethylbenzoyl derivative; it proved to be stable under the conditions of the reduction

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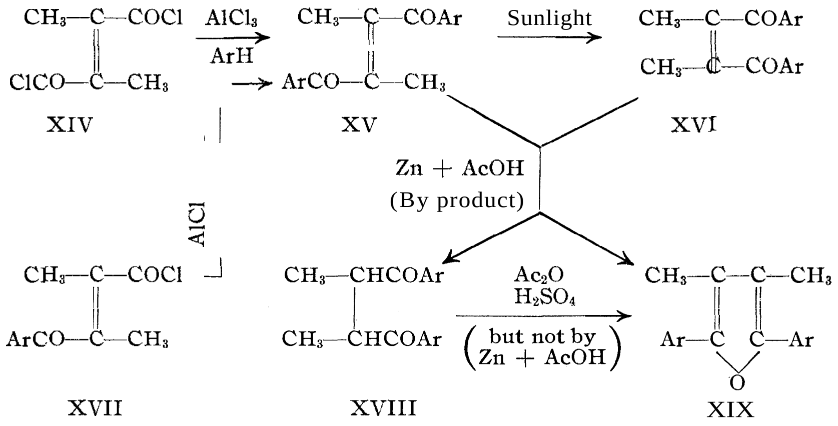
(5) Lutz, THIS JOURNAL, 62, 3423 (1930).

(6) Conant and Lutz, *ibid.*, 45, 1303 (1923).



Ar = aromatic radical, phenyl or mesityl.

as was shown in a separate experiment; but it was very easily converted into the furan by treating with acetic anhydride and a trace of concd. sulfuric acid. The saturated 1,4-diketone is not an intermediate in the reaction since it is stable under these conditions. The formation of the furan can best be accounted for by the spontaneous dehydration of an intermediate dienol, $ArC(OH)=C(CH_3)C(CH_3)=C(OH)Ar$, XX, which is postulated in the theory of 1,6-addition of hydrogen to unsaturated 1,4-dicarbonyl types. A full discussion of this evidence has been given in an earlier paper.[7] The fact that both the cis and *trans* isomers are reduced to the same products (the furan and only one of the two possible saturated 1,4-diketones) in *almost exactly the same ratio,* would be difficult to explain on the basis of simple addition of hydrogen to the ethylene linkage, but is easily accounted for by assuming the intermediate dienol (XX) in which the double bond responsible for the stereoisomerism has been destroyed.

Experimental Part

Dimethyl Unsaturated 1,4-Ketonic Acids

Cis-2-benzoyl-1,2-dimethylacrylic Acid (II).—The Friedel and Crafts reaction with benzene on dimethylmaleic anhydride in benzene as the solvent gave difficultly hydrolyzable amorphous products containing aluminum. Using carbon disulfide this difficulty was largely eliminated.

Five grams of dimethylmaleic anhydride was added slowly to a well-stirred suspension of 10.6 g. of anhydrous aluminum chloride in 25 cc. of benzene and 25 cc. of carbon disulfide. The red reaction mass was heated for one and one-half hours on the steam-bath. The carbon disulfide layer after hydrolysis in ice gave upon evaporation 4 g. of nearly pure cis acid (49%): cryst. from chloroform; sol. in benzene and hot water; m. p. 94° (corr.); dissolves slowly in cold sodium bicarbonate solution, but rapidly in sodium carbonate; precipitated by acid.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.92. Found: C, 70.72; H, 6.88.

A sample of the *cis* acid, exposed to direct sunlight for three days in chloroform with

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[7] Lutz, THIS JOURNAL, **51**, **3008** (1929).

iodine, was recovered quantitatively unchanged. Using bromine instead of iodine, only unchanged material and non-crystalline resinous by-products were isolated.

The acid chloride was prepared by the action of the calculated amount of phosphorus pentachloride on the *cis* acid. It was a viscous yellow oil which decomposed in attempting distillation under reduced pressure. It hydrolyzed easily to the *cis* acid on standing with water. The Friedel and Crafts reaction on a sample of the oil gave only resinous products from which in one case a small sample (0.05 g.) of an unidentified solid of m. p. 211° was isolated. Varying conditions did not give better results.

Cis-2-benzoyl-1,2-dimethylacrylic Methyl Ester, $C_6H_5COC(CH_3)=C(CH_3)COOCH_3$.—A solution of 12 g. of *cis* acid in 25 cc. of absolute methanol saturated with hydrogen chloride was allowed to stand overnight, and was then decomposed in ice and sodium carbonate and extracted with ether. The ether solution, dried over potassium carbonate, was evaporated. The bulk of the residual oil distilled at 163–164° (9 mm.) in a yield of 10.3 g. (77%), and solidified on cooling: cryst. from 70% ethanol, m. p. 53° (corr.).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.52; H, 6.47. Found: C, 71.42; H, 6.38.

A sample of the ester, exposed to direct sunlight in chloroform with iodine for fifteen hours, was recovered quantitatively unchanged.

Hydrolysis.—One gram of the ester was allowed to stand overnight in 10 cc. of 95% ethanolic sodium hydroxide (1 equiv.). The product was isolated by diluting the solution with water and extracting with ether; yield 0.88 g. (94%) of nearly pure *cis* acid.

Trans-2-benzoyl-1,2-dimethylacrylic Acid (**VI**).—The ethyl ester (1 g.) was treated with 13 cc. of a 70% ethanol solution of 0.22 g. of sodium. The mixture was allowed to stand for twenty hours, was then diluted with water, acidified and extracted with ether; yield of nearly pure material 0.83 g. (94%); cryst. from benzene; m. p. 119° (corr.); sol. in hot water; dissolves quickly in sodium bicarbonate solution.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.92. Found: C, 70.54; H, 6.09.

Trans-2-benzoyl-1,2-dimethylacrylic Methyl Ester (**V**).—Dimethylfumaric monomethyl ester mono-acid chloride (6.5 g.) was added to a well-stirred suspension of 8 g. of aluminum chloride in 50 cc. of benzene. The yellow reaction mixture was heated on a steam-bath for twenty minutes, and was decomposed in ice and hydrochloric acid in the usual way. The benzene layer was dried with anhydrous sodium sulfate and distilled at 4.5 mm. pressure, the bulk of the product boiling at 139–143°; yield, 6.5 g. (81%); colorless oil, b. p. 141° (corr.) at 5 mm.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.52; H, 6.47. Found: C, 71.42; H, 6.52.

Hydrolysis of 2 g. in 15 cc. of an ethanol solution of 0.22 g. of sodium gave 1.06 g. (57%) of *trans* acid.

Hydrolysis and Rearrangement of **Trans-benzoyldimethylacrylic** Methyl Ester.—The *trans* ester (0.9 g.) was treated with 10 cc. of absolute ethanol containing 0.15 g. of dissolved sodium. Crystals appeared during the twenty-four hours of standing. The mixture was then diluted with water, acidified and extracted with ether. The acidic products were extracted from the ether by sodium carbonate and liberated by acidification as an oil which crystallized. It was recrystallized from water, to yield 0.3 g. of nearly pure cis-benzoyldimethylacrylic acid which was identified by mixed melting point. No trace of the *trans* acid was detected. The balance of the material was accounted for as an oil which did not crystallize.

A sample of trans-benzoyldimethylacrylic acid under identical reaction conditions was recovered quantitatively unchanged.

Trans-2-benzoyl-1,2-dimethylacrylic Ethyl Ester, $C_6H_5COC(CH_3)=C(CH_3)COOC_2H_5$.—Prepared in the same way as the methyl ester, starting with dimethylfumaric monoethyl acid ester; colorless oil, b. p. 120° (corr.) at 2 mm.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.37; H, 6.95. Found: C, 72.18; H, 6.94.

Hydrolysis of 1 g. of the ester in absolute ethanol with one equivalent of sodium ethylate gave an oily product from which steam distillation gave 0.45 g. of yellow oil which probably contained ethyl phenyl ketone (characteristic odor), although isolation of its oxime failed. From the residue on acidification and extraction with ether 0.07 g. of crude cis-benzoyldimethylacrylic acid was isolated, recrystallized, and identified by a mixed melting point. No *trans* acid was detected.

Trans-2-benzoyl-1,2-dimethylacrylyl Chloride (**XVII**).—The *trans* acid (0.5 g) was treated with the calculated amount of phosphorus pentachloride The oily reaction mixture, without isolating the acid chloride, was subjected to the Friedel and Crafts reaction with benzene and aluminum chloride, following the usual procedure.* An oil was obtained from which 0.08 g. of pure dibenzoyldimethylethylene was isolated and identified by a mixed melting point.

The acid chloride and phosphorus oxychloride mixture from 0.5 g. of acid was heated for one hour with 0.7 g. of aluminum chloride. Upon hydrolysis of the red reaction product, 0.17 g. of pure *trans* acid was recovered and identified.

A sample of the acid chloride in contact with water was hydrolyzed to the acid in less than one hour.

Trans-2-(2,4,6-trimethylbenzoyl)-1,2-dimethylacrylic Acid (XU).—The Friedel and Crafts reaction on dimethylmaleic anhydride with mesitylene was run on a small scale to ensure complete reaction and to avoid long continued heating, which results in the formation of complex resinous products containing aluminum.

Five grams of dimethylmaleic anhydride was added slowly to a well-stirred mixture of 10.6 g. of aluminum chloride in 6 g. of mesitylene and 50 cc. of carbon disulfide. The red viscous reaction mixture was heated for one hour on the steam-bath, and was decomposed in ice and hydrochloric acid. The carbon disulfide layer on evaporation gave a resinous mass which crystallized from benzene and gave 6 g. (61.5%) of nearly pure product; cryst. from benzene; colorless; m. p. 169.5" (corr.); sol. in chloroform, insol. in water.

Anal. Calcd. for $C_{15}H_{18}O_3$: *C*, 73.13; H, 7.37. Found: C, 73.07; H, 7.41.

The acid chloride was obtained as a yellow oil by the action of phosphorus pentachloride on the acid. It decomposed when distillation under reduced pressure was attempted. It was isolated by extracting a petroleum ether solution with water to remove phosphorus oxychloride, and evaporating the petroleum ether in *vacuo.* **A** sample was hydrolyzed slowly in contact with water to the acid which was identified. The Friedel and Crafts reaction was attempted under a variety of conditions in petroleum ether and in carbon disulfide, but the formation of the expected diketone was not observed in any case.[9] In one experiment a small amount of a colorless solid of m. p. 198–199° (corr., decomp.), crystallizing from benzene, was obtained. It gave an analysis of C, 77.81; H, 7.42. We did not have sufficient material for further study.

Trans-2-(2,4,6-trimethylbenzoyl)-1,2-dimethylacrylic Methyl Ester (**XIII**).—The ester was obtained in a rather poor yield in a typical Friedel and Crafts reaction with mesitylene and dimethylfumaric monomethyl ester monochloride, in carbon disulfide. It was best prepared by esterification of the acid

A solution of 10 g. of the acid in absolute methanol was saturated with hydrogen chloride and allowed to stand for twenty-four hours. It was then decomposed in iced sodium carbonate and extracted with ether. Upon distillation yellow oils were obtained

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(8) The phosphorus oxychloride does not interfere in these reactions (see Ref. 7).

(9) This does not necessarily mean that the acid chloride is not of the normal type, however, since the Friedel and Crafts reactions on *trans*-trimethylbenzoylacrylyl chloride and the corresponding monomethyl derivative[2] give only very small yields of the diketones.

which partly crystallized to give a total of 4.4 g. (41%) of nearly pure ester; **cryst.** from alcohol. m. p. 83" (corr.).

Anal Calcd. for $C_{16}H_{20}O_3$: C, 73.80; H, 7.74. Found: C, 73.52; H, 7.49.

One gram of ester in 15 cc. of alcoholic sodium hydroxide (one equiv.) war, hydrolyzed completely in forty-eight hours. The product (0.35 g., 37%) was isolated in the usual way and identified as the original acid.

Trans-2-(2,4,6-trimethylbenzoyl)-1,2-dimethylacrylic Ethyl Ester, $(CH_3)_3C_6H_2$-$COC(CH_3){=}C(CH_3)COOC_2H_5$.—Prepared by adding 10 g. of dimethylfumaric monoethyl ester mono-acid chloride to a well-stirred suspension of 9.5 g. of aluminum chloride in 50 cc. of carbon disulfide and 8.5 g. of mesitylene The red reaction mass was heated for one hour at 40–45° and decomposed in ice and hydrochloric acid in the usual way. The carbon disulfide solution was dried over sodium carbonate, evaporated, and the oily residue distilled under reduced pressure; 7.9 g. of pale yellow oil (55%) was obtained; b. p 131–133° (corr.) at 2 mm.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.40; H, 8.09. Found: C, 74.04; H, 8.10.

One gram of the ester was hydrolyzed by standing in 60% alcoholic sodium hydroxide (one equiv.). On diluting the solution with water and extracting with ether the non-acidic by-products were removed. From the aqueous solution on acidification and extraction with ether, an oil was obtained which partly solidified, giving a yield of 0.3 g. (22%) of nearly pure trimethylbenzoyldimethylacrylic acid.

Dimethyl Unsaturated 1,4-Diketones

Trans-2,3-dibenzoylbutene-2 (Dibenzoyldimethylethylene) (XV).—Dimethylfumaryl chloride (25 g.) was added over a period of half an hour to a well-stirred suspension of 41.5 g. of anhydrous, finely ground aluminum chloride in 200 cc. of dry benzene. The cream colored mixture was stirred with heating on a steam-bath for twenty minutes and the viscous mass hydrolyzed in ice and hydrochloric acid. Upon concentrating the benzene layer successive crops of nearly pure diketone were obtained; yield 31 g. (85%); cryst. from benzene; sol. in chloroform. diff. sol. in ethanol; m. p. 139.5° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.51; H, 6.05.

Samples exposed to direct sunlight in absolute alcohol, benzene, acetone, and ethyl acetate gave only unchanged material and non-crystalline by-products. From benzene a small amount of an unidentified substance was isolated (m. p. 175"). From absolute ethanol a small yield (about 10%) of a colorless solid of m. p. 103" was isolated (*Anal.* C, 78.15, 78.25; H, 7.76, 7.68).

Short refluxing of the diketone with sodium methylate solution gave resinous products.

Solutions of the diketone in acetic acid or chloroform reacted slowly in the sunlight with bromine, liberating hydrogen bromide and giving resinous products.

The diketone dissolved quickly in 40% hydrogen bromide in acetic acid, and a new product containing halogen appeared as colorless needle crystals of m. p. 113" (corr.). The new substance appears not to be a simple addition compound since refluxing for four hours in alcohol with potassium acetate produced no change.

2,5-Diphenyl-3,4-dimethylfuran (XIX).—A well-stirred solution of 2 g. of *trans*-dibenzoyldimethylethylene in 50 cc. of hot glacial acetic acid was treated with 5 g. of zinc dust, and the mixture heated with stirring for twenty minutes. The solution was filtered, cooled, and diluted with water. The oil which precipitated crystallized on standing and was filtered off; yield 1.8 g. Fractional crystallization from alcohol gave the less soluble furan in a yield of 0.62 g. (33%). (The rest of the solid product, probably consisting of a mixture of the two theoreticaliy possible ethanes, will be investigated later.) It was crystallized from ethanol; m. p 116° (corr).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.05; H, 6.50. Found: C, 87.05, 86.63; H, 6.78, 6.55.

Trans - 2,3 - di - [2,4,6 - trimethylbenzoyll - butene - 2 (Di - [trimethylbenzoyl)-dimethylethylenel (XV).—Dimethylfumaryl chloride (25 g.) was added to a well-stirred mixture of 41.5 g. of anhydrous aluminum chloride and 34 g. of mesitylene in 200 cc. of carbon disulfide over a period of one hour and the mixture then heated for two hours on a steam-bath, and hydrolyzed in the usual way. The carbon disulfide solution on evaporation gave successive crops of nearly colorless diketone in a yield of 41.9 g. (87%) as cream tinted crystals melting to a yellow liquid; cryst. from benzene as rhombic plates; m. p. 174.5° (corr.); sol. in chloroform; slightly sol. in alcohol.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 82.71; H, 8.10. Found: C, 82.65; H, 8.06.

On standing in 40% hydrobromic acid in acetic acid a colorless, viscous, oily, insoluble addition product separated.

Cis - 2,3 - di - [2,4,6 - trimethylbenzoyll - butene - 2 (Di - [trimethylbenzoyl)-dimethylethylene] (XVI).—A solution of 5 g. of the *trans* isomer in 50 cc. of benzene was exposed to direct sunlight for two weeks. The oily product was separated by a laborious series of fractional crystallizations from alcohol into an oil, unchanged material, and 2 g. of the *cis* isomer which was recrystallized from alcohol as elongated flat plates; m. p. 149° (corr.).

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.71; H, 8.10. Found: C, 82.40; H, 8.18.

The *cis* isomer proved to be stable when exposed to sunlight in benzene with a trace of iodine, and was recovered with slightly lowered melting point.

When warmed with aluminum chloride in carbon disulfide or benzene, the mixture turned black, and on hydrolysis only resinous products were obtained.

2,5-Dimesityl-3,4-dimethylfuran (XIX).—*Trans*-di-[trimethylbenzoyl]-dimethylethylene (2 g.) was reduced by heating in acetic acid for fifteen minutes with zinc dust. The product was isolated by filtering and diluting with water. The crystalline precipitate was extracted with ether. Upon concentrating, the ether solution deposited 0.18 g. of di-[trimethylbenzoyl]-butane (see below). The solution was then allowed to evaporate to dryness in a glass dish. The bulk of the product (the furan) crawled up the sides and crystallized, leaving a small powdery deposit on the bottom which was easily scraped out and separated from the bulk of material. This latter deposit was digested with a small amount of ether and gave 0.1 g. of the ether-insoluble di-[trimethylbenzoyl]-butane. The ether soluble furan, 1.5 g. (80%) was recrystallized from alcohol, in which it is moderately soluble hot as large thin diamond-shaped plates; m. p. 144° (corr.).

Anal. Calcd. for $C_{24}H_{28}O$: C, 86.72; H, 8.49. Found: C, 86.88; H, 8.75.

In a similar reduction of 0.05 g. of the *cis* diketone, using the same procedure for working up the products, 0.004 g. (8%) of di-[trimethylbenzoyl]-butane and 0.043 (90%) g. of dimesityldimethylfuran were isolated nearly pure and identified by mixed melting points. These percentages are practically the same as the crude yields from the reduction of the *trans* isomer. If the yield of the crude furan in this case were corrected for the small amount of the di-[trimethylbenzoyl]-butane present, the yields of pure products would coincide also.

2,3-Di-(2,4,6-trimethylbenzoyl)-butane (XVIII).—The ether-insoluble fraction from the above reduction of the *trans* diketone (0.28 *g.*, 15%) was difficultly soluble in hot alcohol from which it crystallized as thin diamond-shaped plates of m. p. 191.5–192" (corr.).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.23; H, 8.63. Found: C, 82.45; H, 8.70.

A small sample of the pure product was refluxed in acetic acid with zinc dust for fifteen minutes and was recovered unchanged; 0.035 g. was treated with acetic anhydride and a droplet of sulfuric acid on the end of a glass rod. The difficultly soluble diketone dissolved immediately and new crystals appeared. The mixture was warmed to bring everything into solution and then cooled, allowed to crystallize, and filtered; yield 0.02 g. of nearly pure dimesityldimethylfuran of m. p. 134–140°; identified by recrystallization and mixed melting point.

Summary

The synthesis and preliminary study of *cis* and *trans* benzoyldimethylacrylic acids is reported. The inversion of the *trans* isomer to the *cis* under the influence of alkali is discussed.

Diaroyl-dimethylethylenes have been synthesized from dimethylfumaryl chloride.

The 1,6-addition of hydrogen to *cis* and *trans* di-trimethylbenzoyldimethylethylene is discussed.

UNIVERSITY, VIRGINIA

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Effect of Strong Ultraviolet Irradiation upon the Toxicity of Pure Nicotine

BY GLEN WAKEHAM AND CLARENCE B. JOHNSTON

Two years ago A. J. Pacini and Hugh McGuigan[1] reported that the toxic action of nicotine upon frogs was destroyed by ultraviolet irradiation. Some time later, George P. Tracy, working with the senior author of the present paper (G. W.), demonstrated that while the toxic effects of nicotine upon albino rats can be considerably diminished by ultraviolet irradiation they are by no means destroyed.[2] At the same time it was shown that irradiation beyond the optimum time of exposure will almost completely restore the original toxicity of the nicotine. The work recorded in the present paper is an attempt to ascertain whether any reasonable amount of ultraviolet irradiation will destroy the toxic effects of nicotine upon albino rats.

Experimental

The source of irradiation used was a carbon arc for which the makers claim an intensity in the ultraviolet region forty times that of the ordinary mercury vapor lamp. This claim was approximately verified. In the work earlier reported[2] an irradiation of seventy-five minutes was required, under the mercury vapor lamp, at a distance of ten centimeters, to produce the maximum detoxication. At a distance of fifteen centimeters from the carbon arc the maximum detoxication effects were obtained by irradiation periods of three or four minutes.

In the first series of experiments here recorded, pure, freshly redistilled nicotine was irradiated, in quartz-glass tubes, at a distance of fifteen centimeters from the arc, for periods of from one to sixty minutes. The layer of nicotine (water-clear) was about

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(1) Pacini and McGuigan, *J. Pharmacol.*, 33, 241 (1930)

(2) Wakeham and Tracy, ibid., 44, 295 (1932).

one millimeter deep. The maximum period of exposure (sixty minutes) was at least equivalent to fifteen hours of irradiation at a distance of ten centimeters from an ordinary mercury vapor lamp.

In the second series of experiments a one per cent. solution of nicotine was exposed in open petri dishes to the carbon arc at a distance of twenty-five centimeters. The layer

TABLE I

DATA OBTAINED WHEN PURE NICOTINE WAS IRRADIATED AND ADMINISTERED HYPODERMICALLY IN A ONE PER CENT. SOLUTION

Rats in group	Irradiation, minutes	Range of dosage in mg. per kg. of rat wt.	Number of rats killed	Number of rats surviving	Highest non-lethal dose	Lowest fatal dose
17	0	12.3–29.1	8	9	23.3	15.6
6	1	15.7–39.2	2	4	23.1	28.6
4	1½	14.7–33.6	2	2	28.9	32.0
6	2	18.0–35.7	2	4	31.9	31.2
8	3	14.7–40.7	4	4	26.3	28.4
5	4	25.0–32.4	2	3	30.8	25.4
11	5	16.7–43.5	5	6	40.0	31.0
7	10	19.2–35.1	3	4	25.3	24.6
5	20	18.6–30.0	3	2	20.6	19.0
6	60	19.1–22.0	2	4	21.0	20.5

TABLE II

DATA OBTAINED WHEN A ONE PER CENT. SOLUTION OF NICOTINE WAS IRRADIATED AND ADMINISTERED HYPODERMICALLY

Rats in group	Irradiation, minutes	Range of dosage in mg. per kg. of rat wt.	Number of rats killed	Number of rats surviving	Highest non-lethal dose	Lowest fatal dose
4	1	20.0–28.0	2	2	28.0	25.0
5	2	20.0–33.8	2	3	28.5	25.0
6	3	20.0–33.3	2	4	31.5	32.4
6	4	15.2–24.2	3	3	18.1	17.1
3	5	16.6–24.6	1	2	23.0	24.6
4	10	19.8–22.5	3	1	21.3	19.8
8	20	19.8–31.1	3	5	31.1	22.0
4	60	20.8–24.6	2	2	24.6	20.9

TABLE III

DATA OBTAINED WHEN RATS WERE REPEATEDLY INJECTED WITH "CRITICAL" DOSES OF NICOTINE, BOTH RAW AND IRRADIATED. DOSES ARE GIVEN IN MG. PER KG. OF RAT WEIGHT, INTERVAL IN DAYS. WEIGHTS OF RATS GIVEN IN GRAMS

Rat no.	Rat wt.	Dose	Interval	Dose	Interval	Dose	Interval	Dose	Interval	Dose	Interval	Dose	
11	128	21.5	13	21.5	3	22.7	died						
4	152	21.4	3	21.8	died								
15c	140	28.5	3	26.7	died								
16c	160	25.0	18	23.1	3	26.3	died						
7	82	15.2	3	17.1	3	15.2	3	15.0	died				
6	88	22.7	3	22.7	3	20.6	3	22.2	died				
5	90	16.7	2	16.3	3	16.2	3	17.6	4	17.1	died		
2	116	17.2	2	19.4	died								
23	120	20.8	13	22.5	3	18.4	3	21.2	4	21 9	7	25.8	lived
13	120	16.6	8	14.9	7	17.9	died						
2a	112	17.8	8	16.1	3	19.2	4	22.2	lived				

of solution was never more than two millimeters deep. Both pure nicotine and the diluted nicotine turned to a deep, opaque brown color after long irradiation. This effect is commonly ascribed to oxidation, although quantitative determinations by means of silicotungstate precipitation do not reveal any appreciable decrease in the amount of nicotine present It is suggested that the degree and intensity of irradiation used in these experiments greatly exceed what would be practicable in any commercial process for the treatment of tobacco.

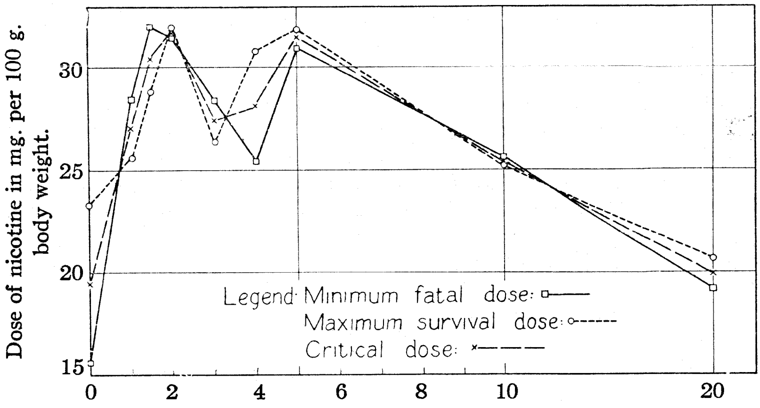

Fig. 1.—Irradiated pure nicotine.

In both series of experiments the nicotine, after irradiation, was injected beneath the loose belly-skin of the rat. The inferences recorded below are based upon what we venture to call the "critical dose," this being the mean of the highest dose which any rat has survived and the lowest dose which has proved fatal. Individual idiosyncrasy is a very disturbing factor in quantitative animal toxicology. Two of the animals used in this work showed resistance to nicotine poisoning so far above the average that the data concerning them were rejected in making out the final diagrams. All doses are calcu-

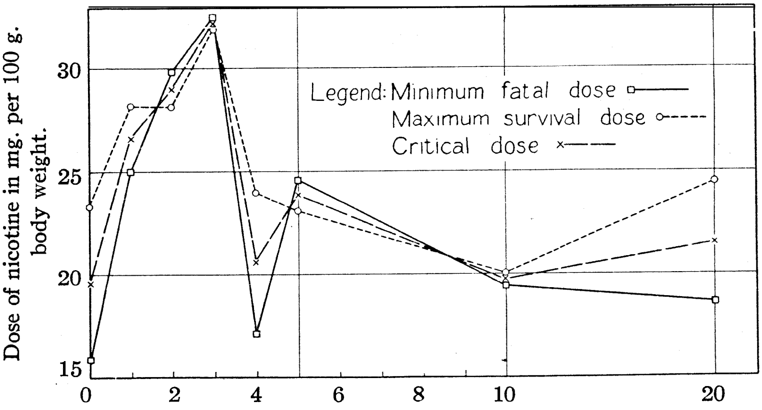

Fig. 2.—Irradiated 1% nicotine solution.

lated in milligrams per kilogram of body weight. No rat was used twice in these experiments, save after an interval of several weeks. Table III presents data which seem to indicate that rats develop neither any marked tolerance nor increased sensitivity when subjected to "critical" doses at short intervals. Some rats succumbed to the second or third "critical" dose. Others maintained good health and gained rapidly in weight even when dosed to death's door every three or four days. Rat No. 23 survived six "critical" doses, and was pensioned.

Doses of nicotine far below the "critical" amount never fail to produce the violent, characteristic nicotine reaction, even when administered repeatedly at short intervals. Nicotine irradiated for certain periods is less toxic than the raw alkaloid, but is always highly poisonous.

Tables I and II give a condensed summary of the data obtained. Charts 1 and 2 are offered, with some hesitation, as the most nearly valid graphical interpretation which could be devised. They represent the general tendencies revealed by the data, although some minor discrepancies are apparent. In order to obtain parallel graphs for the three functions represented, a larger number of animals would have to be used. While it is suggestive that both charts show a second peak in the "detoxication" curve, this may not be significant. The data obtained for sixty-minute periods of irradiation are not included.

Results

It appears from this work that no reasonable amount of ultraviolet irradiation will destroy the toxicity of nicotine. The earlier observation[2] that the partial detoxication obtained by controlled irradiation is restored by over-irradiation, is confirmed.

Albino rats, when subjected to repeated heavy doses of nicotine, develop neither marked tolerance nor susceptibility.

Summary

Intense ultraviolet irradiation, even for long periods, does not destroy the toxicity of pure nicotine.

BOULDER, COLORADO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

A Study of the Reactions between Citric and Acetylsalicylic Acids

BY A. J. DIETZLER AND R. E. NELSON

Introduction

The purpose of this research was to effect a chemical combination, which might be of therapeutic value, between citric acid and acetylsalicylic acid.

Previous Work.—F. Zernik[1] prepared a disalicylic acid ester of methylene citric acid which was marketed under the trade name of Novaspirin. Lehman[2] describes this product as a mild form of aspirin which can be easily administered and borne by the patient; its action, too, is claimed to be more rapid.

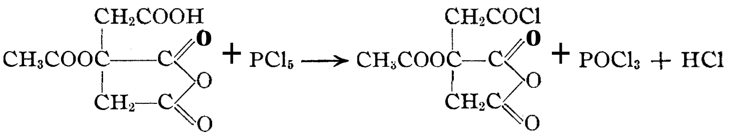
Berendes and Calleen[3] prepared succinyl-disalicyclic acid which is claimed to possess the same desirable therapeutic properties.

Salicylic monoglycol esters[4] and glyceryl esters[5] have been prepared

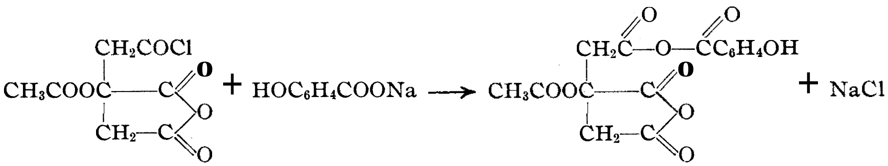
Discussion

Since it was desired to prepare a compound which would contain one mole of salicyclic acid or acetylsalicyclic acid and one mole of citric acid, it seemed best to change in some way three of the four functional groups of citric acid and at the same time block off the alcoholic group.

For this reason acetylcitric acid anhydride was prepared.[6] This was allowed to react with phosphorus pentachloride in order to prepare the acid chloride in the following way



The acid chloride was treated with sodium salicylate with the expectation that the reaction would go as follows



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(1) Zernik, *Apoth. Ztg.*, 22, 508 (1907).

(2) Lehman, *Deut. med. Wochschr.*, 33, 385–386 (1907).

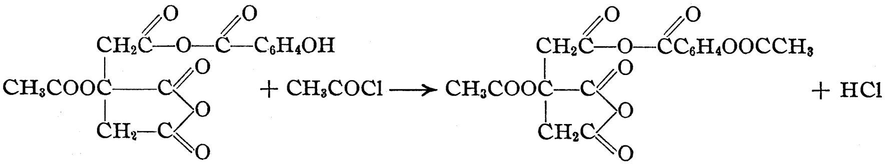
(3) Berendes and Calleen, German Patent 874,929, December 31, 1907.

(4) Badische Anilin und Soda Fabrik, German Patent 173,776, April 21, 1905.

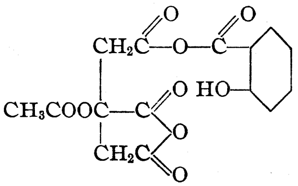
(5) Serger, German Patent 186,111, January 16, 1906.

(6) Klingemann, Ber., 22, 984 (1889).

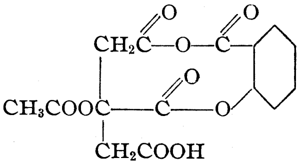
A reaction took place quite readily. After checking the compound by a quantitative saponification and a molecular weight determination, it was planned to acetylate it according to the following reaction



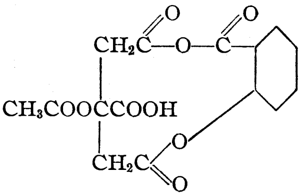
However, no acetylation took place and upon making a ferric chloride test for a phenol, negative results were obtained until the compound had stood for eight minutes in an aqueous solution at room temperature. This showed that there was no free phenol group in the compound and it could not have the structure represented by I. While (I) may have been first obtained, it rearranged into either (II) or (III) which have the same molecular weight.



I



II



III

The rate of hydrolysis of this compound was then determined in 0.0987 N hydrochloric acid at 38°. The products of this hydrolysis were acetic acid, citric acid, salicyclic acid and some aconitic acid. The results of the hydrolysis are shown in Table I.

It was found that after standing for five weeks in a well-stoppered bottle, the compound had a slight acetic acid odor and its melting point had decreased. A single recrystallization of the compound brought its melting point up to the original value. Thus it was evident that on standing some decomposition had taken place.

In attempting to form a combination between citric acid and acetylsalicylic acid many other reactions were tried. They will be briefly outlined and the products given as a matter of record.

1. Anhydrous citric acid was treated with an equivalent amount of acetylsalicylyl chloride in the presence of dimethylaniline. Salicylic acid.

acetylsalicylic acid and citric acid were obtained. They were formed by the addition of water at the end of the experiment.

2. Unsuccessful attempts were made to add acetylsalicylic acid to the double bond in aconitic acid both in the presence of zinc chloride and in the presence of a 2% sulfuric acid solution.

3. 2-Bromo-1,2,3-propanetricarboxylic acid was treated with sodium salicylate in ethereal solution. The products were sodium salicylate, sodium bromide, salicylic acid and aconitic acid.

4. Acetylsalicylyl chloride was treated with anhydrous citric acid. The reaction proceeded smoothly at 110° with the evolution of hydrogen chloride. An uncrystallizable gum was obtained. After standing for two months in a soda lime desiccator some crystals appeared. Analysis showed the presence of acetic, salicylic, citric and aconitic acids.

5. When alkaline citrates were used corresponding products resulted.

6. The sodium alcoholate of triethyl citrate was treated with acetylsalicylyl chloride in boiling ether. The quantitative amount of sodium chloride was obtained. Acetylsalicylic acid was recovered from the gum-like product. The residue reduced alkaline potassium permanganate and was probably triethyl aconitate.

7. In order to verify the results of the last experiment the triethyl ester of 2-chloro-1,2,3-propane-tricarboxylic acid was allowed to react with sodium salicylate in ethereal solution. A sirup was formed which was separated into salicylic acid and triethyl aconitate.

8. Direct esterification between acetylsalicylic and citric acids by means of esterification catalysts was attempted but the experiments were unsuccessful.

Experimental

Reaction of the Acid Chloride of Acetylcitric Acid Anhydride with Sodium Salicylate

Preparation of the Acid Chloride.—Forty grams (1 mole) of acetylcitric acid anhydride, 100 cc. of anhydrous petroleum ether and 38.4 g. (1 mole) of phosphorus pentachloride were mixed and warmed with stirring to about 25° on a water-bath until the evolution of hydrogen chloride had ceased. It was then filtered and the residue on the filter was washed with dry petroleum ether to remove the last trace of phosphorus oxychloride. The product was then recrystallized from chloroform and petroleum ether, m. p. 92–93°; yield 90%.

Anal. Calcd. for $C_8H_7O_6Cl$: Cl, 15.12. Found: Cl, 15.05.

Forty-one grams (1 mole) of the acid chloride of acetylcitric acid anhydride was dissolved in 200 cc. of chloroform and treated with 27 g. (1 mole) of sodium salicylate. The reaction was carried out at room temperature with rapid stirring until all the sodium salicylate was used.

The reaction mixture was then filtered and the residue taken up in 200 cc. of dry acetone. The acetone solution was filtered and the acetone removed from the filtrate under reduced pressure. The slightly brown residue was recrystallized from an acetone–chloroform mixture. A white crystalline compound was obtained, m. p. 162–163°; yield, 57.3%.

The molecular weight by elevation of the boiling point of pure acetone was 339 and 343 and as determined by a quantitative saponification was 335. The molecular weight calculated for $C_{15}H_{12}O_9$ was 336.

Attempted **Acetylation** of this Compound.—Eight grams of the above compound was boiled for three hours with 20 cc. of acetyl chloride but only a trace of hydrogen chloride was evolved. The acetyl chloride was distilled and the residue, after recrystallization, proved to be the original substance.

When 0.10 g. of this compound was suspended in 5 cc. of water, and a drop of 0.10% ferric chloride solution was added no color appeared until eight minutes had passed.

Determination of the Rate of Hydrolysis of this Compound.—Ten separate 0.2000-g. samples of the compound were placed in 150-cc. Erlenmeyer flasks and covered with 10 cc. of 0.0987 N hydrochloric acid. The flasks were stoppered and kept at 38°. At the indicated times the extent of the hydrolysis was determined by filtering a sample, washing the residue twice with water, and titrating the filtrate with 0.135 N sodium hydroxide, using phenolphthalein as the indicator.

The results of these titrations are shown in Table I.

TABLE I

Sample	Time	Cc. of 0.135 *N* NaOH used	% Hydrolysis
1	0 Min.	8.8	6.8
2	15 Min.	9.2	8.6
3	30 Min.	9.6	10.4
4	45 Min.	10.2	13.1
5	60 Min.	12.2	22.2
6	2 Hours	11.7	20.0
7	4 Hours	14.0	30.4
8	24 Hours	19.2	54.0
9	72 Hours	23.0	71.3

After the compound had stood for five weeks in a well-stoppered bottle, it had a slight odor of acetic acid and the melting point had fallen to 152°. The compound was recrystallized from an acetone–chloroform mixture and its melting point was again 162–163°.

Summary

1. General methods of esterification have been tried in an attempt to combine citric acid and acetylsalicylic acid. Esterification was not effected but several interesting mechanisms have been determined.

2. A chemical combination between acetyl citric acid and salicylic acid has been effected.

WEST LAFAYETTE, INDIANA

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Catalysis of Polymerization by Ozonides. II[1]

BY RAY C. HOUTZ AND HOMER ADKINS

A study of the polymerization of dienes in the presence of ozonides led to experimentation directed primarily toward ascertaining: 1, the characteristics of the polymerization of styrene in the presence of ozonides as compared with ihose in the presence of other catalysts; 2, the relative activity of oxygen and ozonides as catalysts for polymerization; 3, whether an interruption of the polymerization process rendered a given polystyrene chain incapable of further addition of styrene.

Experimental Methods

The course of the polymerization was followed in three ways. 1. An aliquot from the reaction mixture of styrene and ozonide was removed from time to time and the viscosity of a 10% solution of it in benzene determined.' 2. Similarly, aliquots (0.5–1.0 g.) of the reaction mixture were dissolved in dioxane (10–15 ml.) and the polystyrene precipitated by the rapid addition of 95% alcohol (150–175 ml.). After one to two days the polystyrene was filtered off, washed and dried to constant weight at 45° (20 mm.) over calcium chloride. (A better separation of polystyrene was obtained with dioxane than with benzene.) The method left less than 2–3% of polystyrene in solution as evidenced by the residue from the evaporation of the alcoholic solution at 50° (20 mm.). **3.** The specific viscosity of the polystyrene so obtained was determined as follows: such a weight of solid was dissolved in benzene as would give a solution containing 26 g. of polystyrene (equivalent to 0.23 mole of styrene) per liter of solution. The flow time of this solution through a viscometer divided by the flow time of benzene gave the relative viscosity. This value less 1 gave the specific viscosity of the polystyrene. Staudinger and associates[2] showed that the specific viscosity of polystyrene is indicative of the size of the molecule and the values have in general been so interpreted in this paper.

Characteristics of Polymerization of **Styrene.**[3]—There are represented in Fig. 1 the typical changes that took place in the viscosity of the solution, in the amount of polystyrene, and in its specific viscosity, during the course of the reaction. It may be seen that for about four weeks there was almost a linear increase in both the amount and specific viscosity of polystyrene formed. The viscosity of the solution increased rather slowly for about three weeks and then much more rapidly for the fourth week.

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(1) Houtz and Adkins, THIS JOURNAL, **53**, 1058 (1931).

(2) Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli, *Ber*., 62, 241 (1929)

(3) *Cf.* Carothers, *Chem. Rev*., **8**, 394 (1931) Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932, pp 157–253.

This is presumably due to the fact that during the earlier period the polymers were not such long chains as they were later, so that a given amount of polymerization produced a much less marked change in the viscosity of the solution. Apparently no more than 92–93% of the styrene underwent polymerization.

The trend of the curve indicating the specific viscosity of the polystyrene is downward after a certain length of time. This is shown more clearly by the data plotted in Fig. 2 for a polymerization at a higher temperature (25°) and with a different catalyst. These data show that while the amount of polystyrene steadily increased to a maximum, the viscosity of the solution and especially the specific viscosity decreased, after reaching a maximum, to approximately 75% of that value.

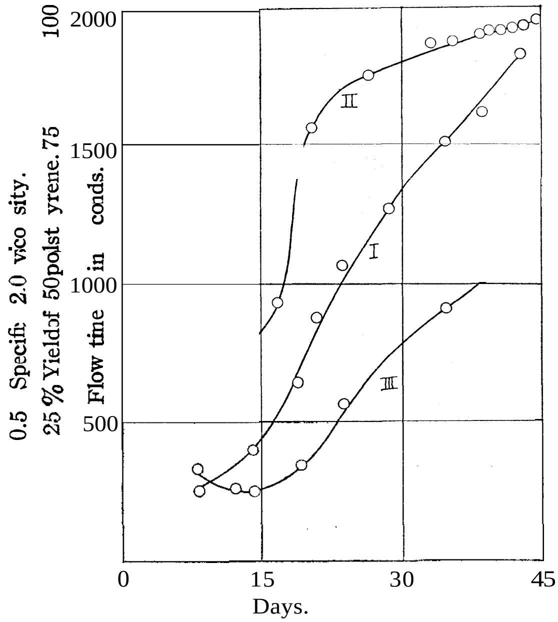

Fig. 1.—Polymerization of styrene at 15° with 2% of diisobutylene ozonide: I, percentage yield of polystyrene; II, flow time of a 10% solution of the reaction mixture in benzene calculated for a viscometer showing a value of 45.7 seconds for benzene; III, specific viscosity of the polystyrene. The data plotted above and in Fig. 2 are for single reaction mixtures; however, all characteristics of the polymerization have been duplicated both under the same conditions and with different catalysts.

The specific viscosity of polystyrene produced varied according to the environment during the reaction. For example, polystyrene produced in an atmosphere of nitrogen at 100° for twenty-two to thirty-two hours had a 19.3, while in oxygen under similar conditions it was 6.6 to 5.2. Under nitrogen but with diisobutylene ozonide or with benzoyl peroxide as a catalyst, the maximum specific viscosity was 1.4 to 1.3. As indicated in Figs. 1 and 2, the specific viscosity rose to a value of approximately 4 in the presence of diisobutylene ozonide as a catalyst at 15°. The polystyrene formed under nitrogen without an added catalyst was quite different in physical properties from other samples of polystyrene. Most of the polystyrene produced under nitrogen could be lifted out on a stirring rod as a tough, doughy mass. Staudinger observed that the specific viscosity of polystyrene decreased with increase in the temperature of formation. He reported values of 5.95 for 15°, 2.18 at 75°, and 1.21 at 115° for polystyrene formed in the absence of an added catalyst.

It should be noted that the samples of polystyrene were not homogeneous with regard to molecular size. If the precipitant (alcohol) was added slowly the polymer first precipitated sometimes had a specific viscosity 150% as great as that of the material precipitated later. Since it was impossible to grind the polymer in a mortar it was advisable to bring about the precipitation very rapidly so that a more representative sample might be obtained for the determination of the average specific viscosity.

Oxygen versus Peroxides and Ozonides as Catalysts for Polymerization.—Staudinger and Lautenschlager[4] reported that oxygen is a much more active catalyst for the polymerization of styrene at 80° than is benzoyl or diphenylethylene peroxide. They state that this is to be expected since oxygen is less available from a peroxide than from the gas. They state that the only way a peroxide could catalyze the polymerization of another compound would be to yield oxygen to it, forming a peroxide of it which would then undergo polymerization. This conclusion is so contradictory to those arrived at in this Laboratory that the matter was tested further. Staudinger and Lautenschlager heated 10-g. portions of styrene at 80° for ten, fifteen, twenty or twenty-five hours with an unspecified amount of oxygen or of benzoyl or diphenylethylene peroxide. They then determined the extent of polymerization by evaporating the excess styrene at 80° in a "high vacuum" for an unspecified length of time. In order to test out their conclusion a series of experiments was performed.

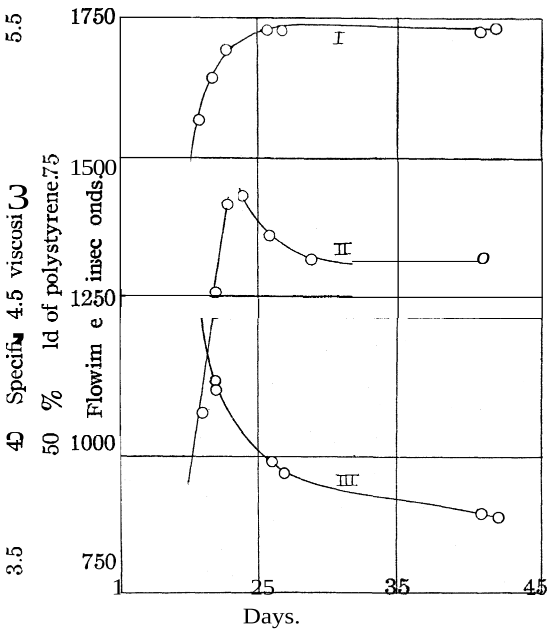

Fig. 2.—The later stages in the polymerization of styrene at 25° with 2% pinene ozonide: I, percentage yield of polystyrene; II, flow time of solution of reaction mixture in benzene; III, specific viscosity of polystyrene.

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[4] Staudinger and Lautenschlager, Ann., 488, 1 (1931).

One-gram samples of styrene were heated at 80° in a thermostat in 20 × 2.5 cm. test-tubes. Before sealing the tubes, they were immersed in an ice–salt mixture, so that an appreciable pressure would be developed on heating to 80°. One tube of each set of six contained oxygen, one carbon dioxide, and the others benzoyl peroxide in three different concentrations (0.1, 1.0, 3.0%) in an atmosphere of carbon dioxide. The volume of each tube was about 60 cc. Considering the initial temperature to be –15" upon sealing there would be 0.078 mole of oxygen available for each mole of styrene if the pressure were to be reduced to one atmosphere in the tube by oxygen absorption. Considering one atom of oxygen in each molecule of benzoyl peroxide to be available, 0.00325 mole of oxygen would be available per mole of styrene, in the tubes containing 0.1% benzoyl peroxide. That is to say, twenty-five times as much oxygen was available to the styrene in the oxygen tube as in the 0.1% benzoyl peroxide tube. Also, since oxygen was bubbled through the styrene immediately before each sample for an oxygen tube was weighed out, free oxygen should have ample opportunity to demonstrate its superiority as a polymerization catalyst. The amount of polymerization under these conditions after ten and twenty hours was as follows: with oxygen 6 and 48%, with carbon dioxide 10 and 15%, with 0.1% benzoyl peroxide 45 and 80%, with 1% benzoyl peroxide 94% at both times. These data show that benzoyl peroxide is a much more active catalyst than oxygen. Other experiments showed that diisobutylene ozonide is much more active than benzoyl peroxide as a catalyst for the polymerization of styrene. Similar results were obtained when the polymerizations were carried out at 25 and 100° in a benzene solution which was vigorously agitated in order to ensure intimate contact of styrene and oxygen.

Another experimental finding may also be noted here, which may have a bearing upon the hypothesis that peroxides and ozonides catalyze polymerization through the liberation of oxygen. Diisobutylene ozonide, for example, did not produce oxygen in any considerable amount when it decomposed. Fifteen grams of the ozonide produced 200 cc. of gas at room temperature within seven days and 500 cc. within a month. The gas analyzed approximately 17% carbon dioxide, 2% unsaturated compounds, 1% oxygen, 23% carbon monoxide, 43% methane and 14% hydrogen.

The stability of diisobutylene ozonide in the presence of unsaturated compounds should be noted. As previously reported this ozonide explodes if heated above about 60° and loses practically all of its catalytic activity if allowed to stand more than four or five days at room temperature. In striking contrast to these statements are the observations that diisobutylene ozonide, dissolved in an unsaturated hydrocarbon, was active as a catalyst for many days at 100°, and with indene at room temperature for several months.[1]

Samples of styrene occasionally vary a great deal with respect to their sensitivity toward polymerization, even when great care is exercised in their preparation and distillation. Samples of styrene which have been in contact with air for some time are very reactive and presumably the high sensitivity toward polymerization is due to the oxygen content. For example, a sample of styrene which had stood for six months in contact with air was as much polymerized after twelve days at 25° in the presence of 4% of its weight of pinene ozonide as was freshly distilled styrene after seventeen days under the same conditions. However, the "old" styrene is not an active catalyst for polymerization, for when 3% of it was added to freshly distilled styrene the resulting mixture polymerized at the same rate as did freshly distilled styrene. Furthermore, polystyrene is not a catalyst for polymerization, for when 1 part of polystyrene was added to 20 parts of freshly distilled styrene the polymerization of the latter was not accelerated.

Addition of Styrene to Polystyrene.—Experiments were conducted with the object of ascertaining whether polystyrene after being precipitated and dried was able to add styrene with the formation of polystyrene of greater molecular weight. To this end samples of polystyrene were prepared, precipitated and dried as in the method described for the gravimetric determination of polystyrene. These samples (*a*, b or c) of polystyrene of known specific viscosity were then mixed with styrene. After an appropriate length of time for reaction the new polystyrenes (d, e or *f*) were precipitated, dried, weighed and their specific viscosities determined. Styrene was allowed to polymerize under exactly the same conditions, the polystyrenes (g, h or *i*) precipitated, weighed and the specific viscosities determined. Mixtures were then made up of polystyrenes (ag, bh and ci) in such a ratio as to be identical with the polystyrenes (d, *e* or *f*) if styrene had not reacted with polystyrene (*a*, b or *c*). The specific viscosities of these mechanical mixtures were then determined. The significant data are recorded in Table I.

If the polystyrene produced from a mixture of polystyrene and styrene had a higher specific viscosity than did the original polystyrene (or the polystyrene produced from styrene alone under similar conditions), then addition of styrene to the original polystyrene *must* have taken place. This is seen to be the case in experiments **1** and **3** of Table I. However, this comparison does not give an accurate indication of the extent of the addition of styrene to polystyrene. Such a comparison may be made between the specific viscosity of the product and of the mechanical mixture referred to above. In experiment 1 the increase was from 11.6 to 15.6, in **3** from 11.5 to 11.9, and in 5 from 2.22 to 2.45. It is thus clear that in all three cases (involving different temperatures, times and catalysts) there was a reaction of styrene with the dried polystyrene.

TABLE I

ADDITION OF STYRENE TO POLYSTYRENE

	Reactants		Time, hrs.	Polystyrene after reaction, g.	% Styrene polymerized	Sp. viscosity	
	Name	g.				Product	Mixture
1	Polystyrene"	0.317	13	0.636[d]	49.7 ± 0.8	15.5 ± 0.12[d]	11.6
	Styrene	.641	(100°)				(ag)
2	Styrene	1.467	13 (100°)	.474[g]	32.4 ± .3	13.0 ± .3	..
3	Polystyrene[b]	0.265	6	.600[e]	28.3 ± .4	11.9 ± .1[e]	11.5
	Styrene	1.181	(100°)				(bh)
4	Styrene	3.290	6 (100°)	.660[h]	20.0 ± .5	11.2 ± .3[h]	..
5	Polystyrene[c]	0.280	72	.359[f]	13.1	2.45 ± .03[f]	2.22
	Styrene	.603	(25")				(ci)
	Pinene ozonide	.024					
6	Styrene	1.808	72	.233[i]	12.9 ± .2	2.43 ± .06[i]	..
	Pinene ozonide	0.054	(25°)				

[a] Specific viscosity 10.5, prepared in 5.5 hrs. at 100° without added catalyst. [b] Specific viscosity 11.5, prepared in 6.0 hrs. at 100° without added catalyst. [c] Specific viscosity 2.20, prepared in 5 days at 25° with pinene ozonide as a catalyst. [d] to [i] See text

Polymerization of Various Compounds.—The catalytic activity of an ozonide in nitrogen for several compounds was tested qualitatively by measuring viscosities before and after standing in contact with the catalyst in sealed tubes. These experiments were carried out chiefly for the purpose of ascertaining whether the catalytic activity of diisobutylene ozonide was limited to non-oxygenated compounds. Benzalacetone in benzene solution with 1% of diisobutylene ozonide showed no viscosity change in seventy days at room temperature, nor in eight days at 100°. A 10% solution of dibenzalacetone in benzene with 1% of diisobutylene ozonide showed a 5% increase in viscosity in eight days at 100°. The blank samples showed no increase. A gummy residue, insoluble in alcohol, was found in the tubes containing the catalyst. Crotonalacetone showed a 205% viscosity increase in eight days with 3% diisobutylene ozonide at 100°, and a 100% increase without catalyst. 2,4-Hexadienal increased in viscosity on heating in air, but 3% of diisobutylene ozonide showed no additional effect. Sorbic acid in dioxane was not affected by the catalyst, either at 23 or at 100°. Ethyl sorbate showed 70% increase in viscosity with 3% pinene ozonide, and 24% increase without catalyst in seventy-six days at 23°. In nine days at 100°, its viscosity increased six-fold without catalyst and ten-fold with 3% pinene ozonide. On heating 1,3-cyclohexadiene at 100° for thirty days a polymer formed which was insoluble in the monomer.[5] There was 50% more gummy residue left after evaporation of the sample containing ozonide than was found in the case of the blank.

(5) Hoffman and Damm, *Mitt schles. Kohlenforschungsinst. Kaiser-Wlhelm Ges.*, *2*, 97 (1925); *Chem. Abstracts*, **22**, 1249 (1928).

Cyclohexene Ozonide.—One of the original objects of this investigation was to ascertain the relative merits of various ozonides as catalysts for polymerization, so the properties of cyclohexene ozonide were investigated. Harries[6] prepared two solid cyclohexene ozonides in carbon tetrachloride solution which he believed to be polymers. In addition to these solid polymers a liquid ozonide of low molecular weight has now been obtained as follows. Ozone was passed into a solution of 6 g. of cyclohexene in 125 cc. of chloroform. An insoluble solid (A) immediately formed. When quantitative absorption of ozone ceased the product was filtered, and the filtrate treated with 2 to 3 volumes of petroleum ether. A granular solid (B) separated which was apparently a mixture, since it melted over a wide range. The insoluble solid (A) was amorphous, paper-like in appearance. It did not dissolve in ether, alcohol, cyclohexane, chloroform, nor acetic acid. It was slightly soluble in benzene and in dioxane. Molecular weight determinations on the soluble solid (B) gave values in benzene of 2100, 2270, 3650, 2185, 2970, 2640; and in dioxane 1515, 1120, 1270, 1200 and 1250. When allowed to stand in a chloroform solution it changed into a substance insoluble in chloroform. Both of these materials (A and B) were found to be practically inactive for the polymerization of styrene, although the (B) solid showed a slight activity toward styrene during a thirty-day interval. When cyclohexene was ozonized in glacial acetic acid, a liquid ozonide (C) was obtained which had a molecular weight of about 450 in freezing dioxane. In nine days at room temperature, 2% of the liquid cyclohexene ozonide (C) in styrene caused the formation of 14.9% polystyrene while 2% of diisobutylene ozonide caused 83.8% of the styrene to polymerize.

Correlation of Results.—The results presented in this paper are in disagreement at two points with those reported by Staudinger and his associates. First, contrary to their observations, peroxides and ozonides have been found to be much more active than oxygen as catalysts for the polymerization of styrene. Second, the polystyrene produced at higher temperatures in this Laboratory in the presence of oxygen had three or four times as large a specific viscosity as did that produced under similar conditions by Staudinger, while the polystyrene produced under nitrogen at 100° had a specific viscosity three or four times as high as the highest specific viscosity observed by him even for polystyrene produced at temperatures as low as 15°. It proved impractical in this Laboratory to polymerize styrene at 15°, for the styrene remained unchanged at room temperatures in contact with air for a year. These results suggest the possibility that the samples of styrene used by Staudinger contained a catalyst which gave a more rapid polymerization and therefore shorter chains than did that used in this Laboratory.

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(6) Harries, *Ann.*, 410, 21 (1915).

A significant fact in regard to the correlation of specific viscosity and length of the polystyrene chain has become evident.[2] The lower specific viscosity of polystyrene produced in thirty-five days as compared with that produced in twenty days (Fig. 2), for example, can hardly be due to a decrease in the length of chain and the breaking of carbon to carbon linkages at 25°, but must rather be due to some other change in dimensions or other characteristics of the polystyrene "molecule." There can be no reasonable doubt that there is, as Staudinger pointed out, a correlation of specific viscosity with length of chain, but at least with the polystyrenes of higher specific viscosity, some other factor apparently in *part* determines the observed value of the latter constant. The specific viscosities referred to in this paragraph are several times as large as those for which Staudinger showed a correlation between specific viscosity and molecular weight.

It appears to the authors that the polymerization of styrene may involve two rather distinct phenomena. The one is the initiation of the reaction or starting of chains, the other is the increase in the length of these chains. It is certain that ozonides, peroxides, salts, etc., catalyze the initiation of chains; however, there is no evidence so far as the authors are aware as to whether or not these catalysts increase the rate of lengthening of these chains. If little catalyst is present the chains become very long even at 100°. If many chains have been begun as in the presence of an active catalyst, then all the available styrene is used up before any of the chains become very long.

The evidence presented in this paper in regard to the capacity of dried polystyrene to add styrene indicates that the polymerization of styrene is not a process that must proceed to completion without interruption. The lengthening of the carbon chain may be stopped by precipitating and drying the polystyrene. The polystyrene will later react with styrene if it is available and the chain thus become longer. In the presence of pinene ozonide there was relatively little addition of styrene to polystyrene or increase in amount of polymerization of styrene in the presence of polystyrene. This is understandable because the catalyst initiated so many chains and the lengthening process is so slow at 25° that by far the greater part of the styrene went to form new chains rather than to prolong those already started.

More styrene reacted within a given length of time in the presence of polystyrene than in its absence, even though polystyrene is not a catalyst for the reaction. This is shown by a comparison of experiments 1 and 2, and 3 and 4 in Table I. In each case approximately 50% more styrene was polymerized in the mixture containing polystyrene than in the mixtures which originally contained no polystyrene. This indicates that the rate of the reaction of styrene is a function of the amount of polystyrene available for addition. All of these facts indicate that the addition of styrene to polystyrene is a normal addition reaction which requires no special hypothesis.

There is no evidence available that seems to the authors to show that the polymerization of styrene by ozonides or peroxides depends upon the transfer of oxygen from the latter to the styrene, or that the decomposition of the ozonide or peroxide is an essential step in the mechanism of polymerization. There is, of course, ample evidence that oxygen does add to alkene linkages and that ozonides polymerize, as shown for cyclohexene ozonide in this paper and as has been previously pointed out by numerous investigators. The role of the ozonide appears on the basis of the experimental results available to be no different from that of a metallic chloride such as tin for the catalysis of polymerization. Presumably the catalysts form a molecular complex with the styrene which is more labile toward polymerization than is styrene alone.

Summary

The course of the polymerization of styrene under a variety of conditions has been followed by determination of the viscosity of the solution and of the weight and specific viscosity of polystyrene produced. The specific viscosity of the polystyrene was shown to reach a maximum after which there was a material decrease in the value of this physical constant. The polystyrene chains of greatest length, as measured by the specific viscosity, were formed under nitrogen at 100°. Certain peroxides and especially diisobutylene ozonide were shown to be a much more active catalysts than oxygen for the polymerization of styrene. Polystyrene after precipitation and drying retained its capacity to add styrene with the formation of chains of greater length. The significance of these facts in regard to the mechanism of catalysis and polymerization of styrene has been discussed. Certain experimental findings in regard to the characteristics of cyclohexene ozonide have been presented. The activity of diisobutylene ozonide for the catalysis of the polymerization of benzalacetone, dibenzalacetone, crotonalacetone, 2,4-hexadienal, ethyl sorbate and cyclohexadiene-1,3 has been demonstrated.

MADISON, WISCONSIN

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

The Grignard Reaction in the Synthesis of Ketones. II. The Preparation of a Series of Mono- and Di-chlorodesoxybenzoins

BY SANFORD S. JENKINS AND EDWIN M. RICHARDSON

In the preceding article[1] a new method of synthesizing desoxybenzoins (benzylphenyl ketones) by means of the Grignard reaction was described. It was found that these compounds could be prepared by the reaction of benzylmagnesium halides with primary benzamides and that quite satisfactory yields were obtained when the reactants, in the ratio of three to four equivalents of the former to one of the latter, were heated over sufficiently long periods of time. Although rearrangements are known to take place when benzylmagnesium halides are treated with certain substances,[2] no evidence of any abnormal product was obtained in this work. By means of the Beckmann reaction[1] the oximated derivatives were transformed into the corresponding anilides, the structures of which were established by comparison with authentic specimens.

In the present article eight mono- and di-chlorodesoxybenzoins, which were prepared and shown to be authentic by the methods outlined above, will be described. Thus by condensing o-chlorobenzamide and benzamide with benzylmagnesium chloride and o-chlorobenzylmagnesium bromide, benzyl o-chlorophenyl, o-chlorobenzyl phenyl and o-chlorobenzyl *o*-chlorophenyl ketones were prepared. In a similar manner benzyl *p*-chlorophenyl,[3] *p*-chlorobenzyl phenyl[4] and *p*-chlorobenzyl *p*-chlorophenyl ketones were obtained from the corresponding amides and Grignard reagents. Finally o- and p-chlorobenzamides were treated with o- and p-chlorobenzylmagnesium bromides to produce o-chlorobenzyl *p*-chlorophenyl and *p*-chlorobenzyl o-chlorophenyl ketones (see Table I for preparational data and constants of the ketones).

Under the conditions of our experiments seven of the ketones produced single oximes which proved to be of the anti-benzyl types. From *o*-chlorobenzyl o-chlorophenyl ketone, however, both the syn- and anti-benzyl ketoximes were obtained. It is quite possible that *syn* types could be prepared from the other ketones as well by suitably varying the conditions. In a later communication we shall describe the results of an extensive investigation dealing with the oximation of desoxy ketones in

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(1) Jenkins, THIS JOURNAL, **55**, 703 (1933).

(2) For references see Austin and Johnson, ibid., 64, 647 (1932); Gilman and Kirby, ibid., **54**, 345 (1932).

(3) Benzyl *p*-chlorophenyl ketone, which was prepared by means of the Friedel–Crafts reaction, and the corresponding oxime have been described by Szego and Ostinelli [*Atti* **111** *congresso naz- chim. pura applicata*, p. 395–401 (1930); cf. C. A., 26, 1524 (1931)]. The compounds, if authentic, were impure, for the melting points given were over 5° too low.

(4) Petrenko-Kritschenko [Ber., **25**, 2239 (1892)] has described the preparation of *p*-chlorobenzyl phenyl ketone but the melting point given was too low.

TABLE I

PREPARATIONAL DATA AND CONSTANTS OF KETONES WITH ANALYSES AND MOLECULAR WEIGHTS

Grignard	Benzamide	Time, hours	Letter	Ketone	Yield, %	Appearance	M. p., (corr.), °C.	Formula	Chlorine, % Calcd.	Chlorine, % Found	Mol. wt. Calcd.	Mol. wt. Found
$C_6H_5CH_2MgCl$	o-$ClC_6H_4CONH_2$	70	A	Benzyl o-chloro phenyl	71	Faint yellow oil	B. p. 176–178 (5 mm.)	$C_{14}H_{11}ClO$	15.37	14.85	230.5	241
o-$ClC_6H_4CH_2MgBr$	$C_6H_5CONH_2$	24	B	o-Chlorobenzyl phenyl	73	Clusters of cream colored needles	70.5	$C_{14}H_{11}ClO$	15.37	15.44	230.5	237
o-$ClC_6H_4CH_2MgBr$	o-$ClC_6H_4CONH_2$	50	C	o-Chlorobenzyl o-chlorophenyl	70	Faint yellow viscous oil	B. p. 195–210 (6 mm.)	$C_{14}H_{10}Cl_2O$	26.76	25.80	265	274
$C_6H_5CH_2MgCl$	p-$ClC_6H_4CONH_2$	14	D	Benzyl p-chloro phenyl	77	Cream colored scales	107.5	$C_{14}H_{11}ClO$	15.37	15.41	230.5	222
p-$ClC_6H_4CH_2MgBr$	$C_6H_5CONH_2$	24	E	p-Chlorobenzyl phenyl	70	Thin colorless plates	138	$C_{14}H_{11}ClO$	15.37	15.23	230.5	240
p-$ClC_6H_4CH_2MgBr$	p-$ClC_6H_4CONH_2$	24	F	p-Chlorobenzyl p-chlorophenyl	74	White needles	114	$C_{14}H_{10}Cl_2O$	26.76	26.86	265	275
o-$ClC_6H_4CH_2MgBr$	p-$ClC_6H_4CONH_2$	65	G	o-Chlorobenzyl p-chlorophenyl	80	Colorless needles	108.5	$C_{14}H_{10}Cl_2O$	26.76	26.69	265	270
p-$ClC_6H_4CH_2MgBr$	o-$ClC_6H_4CONH_2$	40	H	p-Chlorobenzyl o-chlorophenyl	72	White glittering scales	65	$C_{14}H_{10}Cl_2O$	26.76	26.87	265	275

TABLE II

CONSTANTS OF OXIMES AND ANILIDES WITH ANALYTICAL DATA

Letter	Ketoxime	Appearance	M. p. (corr.), °C.	Anilide	Appearance	M. p. (corr.), °C.	Oxime formula	Chlorine, % Calcd.	Chlorine, % Found	Anilide formula	Chlorine, % Calcd.	Chlorine, % Found
A	*Anti*-Benzyl o-chlorophenyl	White prisms	131.5–132.5	Phenylacet-o-chloro-	Fine white matted needles	120	$C_{14}H_{12}NClO$	14.46	14.52	$C_{14}H_{12}NClO$	14.46	14.28
B	*Anti*-o-Chlorobenzylphenyl	White prisms	85–86	o-Chlorophenylacet-	Clusters of fine white needles	140	$C_{14}H_{12}NClO$	14.46	14.38	$C_{14}H_{12}NClO$(5)		
C¹	*Anti*-o-Chlorobenzyl o-chlorophenyl	Balls of cream needles	103–104	o-Chlorophenylacet-o-chloro-	Fine white needles	159.5	$C_{14}H_{11}NCl_2O$	25.30	25.40	$C_{14}H_{11}NCl_2O$	25.30	2
C²	*Syn*-o-Chlorobenzyl o-chlorophenyl	Colorless diamond-shaped plates	145–146	o-Chloro-benzoyl-o-chlorobenzylamine	White needles	111	$C_{14}H_{11}NCl_2O$	25.30	25.43	$C_{14}H_{11}NCl_2O$	25.30	25.40
D	*Anti*-Benzyl p-chlorophenyl	Long colorless glittering needles	122.5–123.5	Phenylacet-p-chloro-	Long thin colorless needles	168	$C_{14}H_{12}NClO$	14.46	14.52	$C_{14}H_{12}NClO$	14.46	14.31
E	*Anti*-p-Chlorobenzyl phenyl	White prisms	95–96	p-Chlorophenylacet-	Colorless prisms	168	$C_{14}H_{12}NClO$	14.46	14.67	$C_{14}H_{12}NClO$(5)		
F	*Anti*-p-Chlorobenzyl p-chlorophenyl	Short white needles	124.5–125.5	p-Chlorophenylacet-p-chloro-	Short white needles	190	$C_{14}H_{11}NCl_2O$	25.30	25.20	$C_{14}H_{11}NCl_2O$	25.30	25.08
G	*Anti*-o-Chlorobenzyl p-chlorophenyl	White prisms	105–106	o-Chlorophenylacet-p-chloro-	Cluster of fine hair-like needles	184	$C_{14}H_{11}NCl_2O$	25.30	25.18	$C_{14}H_{11}NCl_2O$	25.30	25.21
H	*Anti*-p-Chlorobenzyl o-chlorophenyl	Thick white prisms	88–89	p-Chlorophenylacet-o-chloro-	White prisms	171	$C_{14}H_{11}NCl_2O$	25.30	25.15	$C_{14}H_{11}NCl_2O$	25.30	25.40

which certain generalizations will be discussed. For the present, however, we are concerned with this study only as a means of further confirming the structures of the ketones (see Table II).

Experimental

The amides were prepared by refluxing the corresponding acids on the water-bath with double the calculated amount of thionyl chloride until the evolution of hydrogen chloride and sulfur dioxide ceased. The excess of thionyl chloride was then distilled under reduced pressure and the crude acid chlorides poured into ice-cold ammonium hydroxide solution. The resulting amides were purified by crystallization from water. The method is convenient and the yields are satisfactory.

The Grignard reagents were prepared and the condensations carried out according to the method and technique described in article I[1] of this series. In the present work it was found, however, that the yields could be improved and better products (not so yellow) obtained when the condensations were carried out in an atmosphere of hydrogen. Employing this modification the yield of ketone H was increased from 55 to 72%. The yields reported were obtained by treating four equivalents of the Grignard reagents (0.10 to 0.20 mole) to one equivalent (0.025 to 0.050 mole) of the amides. The yields were calculated on the basis of the amides employed and represent the product obtained after one crystallization from alcohol. The melting points of the once crystallized ketones were within two or at most four degrees of the fusing points (see Table I) of the pure compounds.

Ketone B was purified by recrystallization from ligroin (Skellysolve "C"), while D, E, F, G and H were recrystallized from alcohol.

The anilides, as obtained by rearrangement of the oximes, were obtained in yields of 55 to 80%. The structures of these substances were established by mixed melting points with authentic anilides prepared from the corresponding acids and amines.

The oximes listed were all prepared by mixing 1.00 g. of ketone, 1.00 g. of hydroxylamine hydrochloride, 1.60 g. of potassium acetate (dried) and 30 cc. of 95% alcohol. The mixture was allowed to stand overnight and heated on the water-bath under reflux for three hours. To the solution hot water was then added until the potassium chloride dissolved and a faint opalescence appeared. On slowly cooling the oximes usually crystallized without difficulty.

The crude oximes were obtained in yields of 90–99%. Oximes A and F were recrystallized from dilute alcohol (about 80%), while B, D, E, G and H were purified by recrystallization from ligroin (Skellysolve "C"). In order to separate C^1 and C^2 the following method (which may not be the best) was used: the mixture of crude oximes was dissolved in the smallest amount of slightly diluted (about 90%) alcohol and allowed to stand for several days at room temperature. When crystallization appeared to be complete, the oxime was separated and further purified in the same manner. By this means C^2 (*syn*-benzyl isomer) was obtained. The mother liquors were combined and evaporated to dryness under reduced pressure. The solid was then recrystallized from ligroin. This product (C^1) proved to be the anti-benzyl isomer. We are not certain that either of these isomers is entirely pure but each of them was recrystallized until its melting point remained constant. The relative yields of syn and anti isomers seemed to vary with different batches of the crude mixture although the *anti* isomer was always obtained in the greatest percentage.

The oximes were rearranged in the following manner: 0.50 g. of oxime was dissolved in 20 cc. of anhydrous ether and after cooling in an ice-bath the solution was treated with 1.0 g. of powdered phosphorus pentachloride. The mixture was then shaken for five minutes and poured into about 100 cc. of ice water. The ether was evaporated by means of a stream of air, after which the crude anilide was filtered, washed with water and crystallized from alcohol. In the case of oxime C^2 the purest anilide was obtained when the ether solution was refluxed on the water-bath for ten minutes.

For comparison the anilides were prepared independently by heating 0.010 mole weights of the corresponding acids and amines in an oil-bath at 180–200° for two hours The anilides were crystallized from alcohol until pure. Anilides B and E have been described heretofore.[5]

o- and *p*-chlorophenylacetic acids were prepared according to the method of Mehner [5] The nitriles, however, were not purified but were hydrolyzed directly to the acids by refluxing with concentrated hydrochloric acid for four hours.

The o-chlorobenzylamine employed in this work was obtained from *o*-chlorobenzaldoxime according to the method of Franzen.[6] The procedure was considerably shortened, however, by steam distilling the crude amine rather than separating it from the ether solution as the carbonate. The chloroanilines and chlorobenzyl halides employed in this work were purchased from the Eastman Kodak Company.

The molecular weight determinations of B, D, E, F, G and H were made by means of the Rast method[7] using borneol instead of camphor. The Menzies–Wright boiling point method[8] was employed in cases A and C.

The halogen analyses were made by the Parr bomb method.

Ketones **A** and C were not pure as is evidenced by their analyses. Because of the small quantities available (about 8 cc. of each) it was not feasible to purify them further.

Summary

The Grignard method of synthesizing desoxybenzoins, which was described in article I, has been extended.

By condensing primary benzamides with benzylmagnesium halides under suitable conditions a series of eight mono- and di- chloro ketones has been prepared and studied.

In no case was any evidence of an abnormal product observed in this type of Grignard reaction.

Under the conditions of the experiments seven of the ketones produced only anti-benzyl oximes. From o-chlorobenzyl o-chlorophenyl ketone both syn- and *anti*-benzyl ketoximes were obtained.

The oximes were rearranged by the Beckmann method and the structures of the resulting anilides were established.

In the course of this work twenty-one new compounds were obtained and characterized.

BALTIMORE, MARYLAND RECEIVED SEPTEMBER 19, 1932
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(5) Mehner, *J. prakt. Chem.*, 62, 562 (1900).

(6) Franzen, *Ber.*, 38, 1415 (1905).

(7) Rast, *ibid.*, B55, 1051 (1922).

(8) Menzies and Wright, THIS JOURNAL, 43, 2314 (1921).

[CONTRIBUTION NO. 112 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. VIII. α-Alkyl-β-Vinylacetylenes

BY RALPH A. JACOBSON AND WALLACE H. CAROTHERS

Vinylacetylene is a prolific source of new and interesting compounds. The present paper is concerned with homologs of vinylacetylene, which are readily accessible through the mediacy of sodium vinylacetylide.[1] Vinylethinylmagnesium bromide reacts with very active alkyl halides such as triphenylchloromethane,[2] but not with simple alkyl halides. Sodium vinylacetylide on the other hand reacts almost explosively with simple alkyl halides. The reaction can be moderated, however, by employing low temperatures, and when the halide is cautiously added to the acetylide in liquid ammonia it proceeds smoothly and furnishes good yields of the α-alkyl-β-vinylacetylenes. Alkyl sulfates or sulfonates can be used with similar results. The properties of alkyl vinylacetylenes obtained by these methods are indicated in Table I. The compounds are colorless liquids with characteristic odors. On standing they slowly polymerize, yielding viscous, yellow sirups.

TABLE I

PHYSICAL PROPERTIES OF $CH_2{=}CH{-}C{\equiv}C{-}R$

Nature of R	B. p., °C.	d_4^{20}	n_D^{20}	M_R calcd.	M_R found	Exaltation
CH_3	59.2 at 760 mm.	0.7401	1.4496	22.82	23.94	1.12
C_2H_5	84.5–85.3 at 758 mm.	.7492	1.4522	27.44	28.82	1.38
n-C_4H_9	62–63 at 61 mm.	.7830	1.4592	36.68	37.71	1.03
n-C_7H_{15}	74.5 at 9 mm.	.7962	1.4606	50.53	51.65	1.12

Experimental Part

1-Methyl-2-vinylacetylene.—A one-liter, 3-necked flask was fitted with a mercury-sealed stirrer, a dropping funnel, and an exit tube. The exit tube was connected to a vertical condenser which in turn led to a gas-washing train consisting of an empty bottle, a second bottle containing water, and a third containing 10% sulfuric acid. The exit tube from the latter was connected to a calcium chloride drying tower and this in turn led to a receiver immersed in a Dewar flask maintained at −78°.

To a solution of 104 g. of vinylacetylene in 600 cc. of liquid ammonia was slowly added 58.5 g. (1.5 moles) of powdered sodamide. The mixture was stirred for three hours and then concentrated to approximately 300 cc. by evaporating the ammonia in a current of nitrogen; 189 g. (1.5 moles) of dimethyl sulfate was added slowly through the separatory funnel. The reaction was very vigorous and about four hours were required for the addition. The ammonia was allowed to evaporate and the reaction flask was finally heated on a water-bath. Part of the 1-methyl-2-vinylacetylene collected in the first bottle and part in the second. The portions were combined, dried over calcium chloride, and distilled. Some low-boiling material came over first and then 37.6 g (38%) of 1-methyl-2-vinylacetylene was collected. It was a colorless, volatile liquid possessing a powerful hydrocarbon odor somewhat similar to that of vinylacetylene.

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(1) Carothers and Jacobson. THIS JOURNAL, 55, 1097 (1933).

(2) Carothers and Berchet, *ibid.*, 55, 1094 (1933).

Anal. Calcd. for C_5H_6: C, 90.91; H, 9.09. Found: C, 90.97; H, 8.63. Mol. wt. calcd.: 66. Found: 66.1, 66.3 (cryoscopic, benzene).

1-Ethyl-2-vinylacetylene.—A solution of 104 g. (1.5 moles) of vinylacetylene in 500 cc. of liquid ammonia was treated with 58.5 g. (1.5 moles) of powdered sodamide as in the preceding experiment. After three hours, 231 g. of diethyl sulfate was added slowly through the dropping funnel. The mixture was allowed to stand overnight while the ammonia evaporated. Water was added to the reaction flask and the upper layer, weighing 51 g., was separated. After drying with calcium chloride, the liquid was distilled. A small amount of low-boiling liquid came over first, after which 37 g. of 1-ethyl-2-vinylacetylene distilled. The product was a colorless liquid with an odor similar to that of I-methyl-2-vinylacetylene.

Anal. Calcd. for C_6H_8: C, 90; H, 10. Found: C, 89.47, 89.73; H, 10.20, 9.44. Mol. wt. calcd.: 80. Found: 78.4, 79.5 (cryoscopic, benzene).

I-Ethyl-2-vinylacetylene was also prepared by treating sodium vinylacetylide with ethyl *p*-toluenesulfonate according to the method recently employed by Truchet:[3] 58.5 g. (1.5 moles) of sodamide was slowly added to a solution of 104 g. of vinylacetylene in 200 cc. of butyl ether at −10° and the mixture was stirred for three hours. A solution of 300 g. (1.5 moles) of ethyl *p*-toluenesulfonate in 200 cc. of butyl ether was then added drop by drop during several hours. The thick mixture was heated in a water-bath at SO° for three hours and allowed to stand overnight. Water was added but such a troublesome emulsion formed that the mixture was set aside for twenty-four hours in a separatory funnel. The ether layer was separated, dried with calcium chloride, and distilled. A considerable quantity of low-boiling material first distilled, and then a fraction weighing 45 g. and boiling at 78–88" was collected. Upon redistillation 28.5 g. (23.7%) of 1-ethyl-2-vinylacetylene boiling at 84–85° was obtained. Of the two methods of preparing this compound, the first was the better.

1-Butyl-2-vinylacetylene.—A solution of 100 g. of vinylacetylene in 400 cc. of liquid ammonia was treated with 39 g. (1 mole) of powdered sodamide. After three hours, 137 g. (1 mole) of butyl bromide was slowly dropped into the solution during about four hours. The mixture was allowed to stand overnight, water was added, and the upper layer separated. The liquid was dried with calcium chloride and distilled. The product was a colorless liquid with a characteristic hydrocarbon-like odor. The liquid polymerized during the course of three months to a yellow viscous sirup.

Anal. Calcd. for C_8H_{12}: C, 88.88; H, 11.12. Found: C, 88.65; H, 10.76. Mol. wt. Calcd.: 108. Found: 103, 104 (cryoscopic, benzene).

I-Heptyl-2-vinylacetylene.—A solution of 75 g. of vinylacetylene in 400 cc. of liquid ammonia was treated with 39 g. (I mole) of powdered sodamide. After three hours, 150 g. (0.84 mole) of heptyl bromide was slowly added during four hours. The mixture was allowed to stand overnight, water was added, and the upper layer (128 g.) separated. After drying with calcium chloride, the liquid was distilled; 101 g. of 1-heptyl-2-vinylacetylene was collected. Based on the heptyl bromide used, the yield was 80% of the theoretical. On standing for two months the liquid polymerized to a yellow viscous sirup.

Anal. Calcd. for $C_{11}H_{18}$: C, 88.00; H, 12.00. Found: C, 87.65, 87.51; H, 11.55, 11.81. Mol. wt. Calcd.: 150. Found: 143, 145 (cryoscopic, benzene).

Summary

Sodium vinylacetylide reacts with alkyl halides, sulfates, or sulfonates, yielding α-alkyl-β-vinylacetylenes. Compounds of the formula $CH_2=$

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(3) Truchet, *Compt. rend.*, 191, 854 (1930).

$CH—C\equiv C—R$ are described in which R is methyl, ethyl, n-butyl and n-heptyl.

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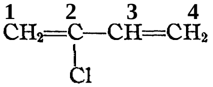
Acetylene Polymers and their Derivatives. IX. 1-Alkyl-2-chloro-1,3-butadienes and their Polymers (Fourth Paper on New Synthetic Rubbers)

BY RALPH A. JACOBSON AND WALLACE H. CAROTHERS

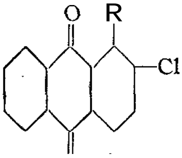
Chloroprene (I) polymerizes very rapidly to form a rubber-like product of excellent quality.[1]



$$\overset{1}{CH_2}=\underset{\displaystyle Cl}{\overset{2}{C}}—\overset{3}{CH}=\overset{4}{CH_2} \quad (I)$$

Replacement of the hydrogen at the 3-position by methyl does not appreciably affect the rate of spontaneous polymerization, but the rubber-like product is somewhat deficient in extensibility.[2] On the other hand, the introduction of methyl at both the 3- and the 4-positions greatly diminishes the tendency to polymerize, and the product, although highly extensible, is lacking in resilience.[2]

The present paper is concerned with chloroprenes in which a hydrogen in the 1-position has been replaced by alkyl. These compounds are readily obtained by the action of hydrogen chloride on the corresponding a-substituted vinylacetylenes. The latter have already been described.[3] Doubtless because of their lesser solubility in water they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon, which reacts practically completely when shaken for five hours at room temperature with two moles of concentrated hydrochloric acid containing cuprous chloride.[4] Under the same conditions a-methylvinylacetylene is less than 40% utilized. Reaction of the higher homologs is still slower, so that elevated temperature was needed for the butyl compound, and the heptyl compound required the addition of alcohol to function as a solvent.



(II)

The physical properties of the new homologs of chloroprene are indicated in Table I. They are colorless liquids with characteristic odors. Like chloroprene, they react with a-naphthoquinone to form addition products, which are readily oxidized to α-alkyl-β-chloroanthraquinones (11),and their identity is established by this reaction.

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(1) Carothers, Williams, Collins and Kirby, THIS JOURNAL, 53, 4203 (1931).

(2) Carothers and Coffman, ibid., 54, 4071 (1932).

(3) Jacobson and Carothers, *ibid.*, 55, 1622 (1933).

(4) Carothers, Berchet and Collins, ibid., 64, 4066 (1932).

No additions to systems of the type $\text{alkyl}-\overset{(1)}{\text{C}}\equiv\overset{(2)}{\text{C}}-\text{CH}=\text{CH}_2$ have been recorded hitherto. It is therefore of interest to observe that the result of adding hydrogen chloride under the conditions described is to place H at (1) and Cl at (2), but in view of the mechanism already established for vinylacetylene[4] it seems probable that the first product is $\text{alkyl}-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{Cl}$, which then rearranges to the substituted chloroprene. In any event, current theories, either empirical or electronic, do not appear to account for this result.

TABLE I

PROPERTIES OF $\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}-\text{R}$

Nature of R	B. p., °C.	Pressure in mm.	n_D^{20}	d_4^{20}	MR Calcd.	MR Found	Exaltation
H[1]	59.4	760	1.4583	0.9563	24.61	25.27	0.66
CH_3	99.5–101.5	759	1.4785	.9576	29.22	30.32	1.10
C_2H_5	68.2–69	117	1.4770	.9390	33.84	35.05	1.21
n-C_4H_9	64–65	18	1.4794	.9366	43.04	43.77	0.73
n-C_7H_{15}	74–76	1	1.4785	.9141	56.93	57.79	0.86

Polymerization of the Substituted Chloroprenes.—Chloroprene polymerizes practically completely to an elastic, rubber-like mass in forty-eight to eighty hours when directly illuminated by a 150-watt Mazda lamp at 30 to 35°. The substituted chloroprenes listed in Table I all polymerize much more slowly. The methyl compound requires about six or seven weeks, and the higher members of the series require still longer times. The products, with the possible exception of that derived from the heptyl compound, are definitely rubber-like but much inferior in quality to polychloroprene. The product from the methyl compound is the best. Polymerization under direct light from a 150-watt Mazda lamp during one month at the ordinary temperature gave a soft mass containing a considerable proportion of unchanged monomer. The polymer precipitated by the addition of alcohol was a soft, plastic mass resembling milled smoked sheets. It was compounded with 10% of its weight of zinc oxide and then heated at 120° for twenty minutes. The plastic properties were quite largely suppressed by this treatment, but the product appeared to be incompletely vulcanized. It was strong and tough and had a high extensibility, but it recovered from stretch rather slowly, and was deficient in resilience. Vulcanizates obtained from higher members of the series were still softer and more deficient in resilience.

Preparation of 1-Alkyl-2-chloro-1,3-butadienes.—The general procedure was similar to that already described for chloroprene.[4] One mole of the hydrocarbon was shaken with approximately 2.2 moles of concentrated aqueous hydrochloric acid containing about 0.25 mole of cuprous chloride and 0.2 mole of ammonium chloride. The non-aqueous layer was separated, stabilized with hydroquinone and distilled; or, in some cases, the reaction mixture was distilled with steam after the addition of hydroquinone. The reaction time varied from five to sixteen hours and the temperature from 23 to

ANALYTICAL DATA FOR THE 1-ALKYL-2-CHLORO-1,3-BUTADIENES

Nature of alkyl	Calculated				Found			Mol. wt. (cryoscopic in benzene)
	C	H	Cl	Mol. wt.	C	H	Cl	
CH_3	58.56	6.83	34.61	102.5	58.49	6.92	34.63	102 103
C_2H_5	61.82	7.73	30.45	116.5	61.64	7.97	30.28	116 119
n-C_4H_9	66.45	8.99	24.56	144.5	65.73	8.76	24.57	152 154
n-C_7H_{15}	70.79	10.19	19.02	186.5	70.39	10.04	19.26	189 193

45°. The product in each case appeared to consist entirely of the substituted chloroprene and the unchanged hydrocarbon. Yields were good, but conversions were not complete. No appreciable addition could be obtained with the heptyl compound in aqueous solution, but a fair conversion was obtained when the hydrocarbon was shaken with 3.4 moles of hydrochloric acid in ethyl alcohol with 0.35 mole of cuprous chloride and 0.44 mole of ammonium chloride for five hours at 70 to 80°.

Condensation of Naphthoquinone with the 1-Alkyl-2-chloro-1,3-butadienes.—The substituted chloroprenes were each heated with α-naphthoquinone in the ratio of about 1 g. to 0.5 g. at 100° for about two hours. Alcohol containing sodium hydroxide was added, and air was bubbled through the resulting suspension. The solids were crystallized as indicated below and were thus obtained in the form of yellow crystals (generally needles).

SUBSTITUTED ANTHRAQUINONES OF FORMULA II

R =	Cryst. from	M. p., °C.	Calcd. C	Calcd. H	Found C	Found H
CH_3	Acetic acid	181	70.19	3.51	70.16	3.50
C_2H_5	Alcohol	151–152	70.99	4.06	70.93	4.18
n-C_4H_9	Methanol	129–130	72.37	5.03	71.83	5.16
n-C_7H_{15}[a]	Alcohol	112.5–113.5	74.02	6.17	74.12	6.40

[a] In this case the intermediate tetrahydro compound was isolated, probably **1-heptyl-2-chloro-4,4a,9,9a-tetrahydro-9,10-anthraquinone**; white crystals from methanol, m. p. 96–98°.

Anal. Calcd. for $C_{21}H_{25}O_2Cl$: C, 73.16; H, 7.26. Found: C, 72.48; H, 7.44.

Polymerization of the I–Alkyl–2–chloro–1,3–butadienes

1-Methyl-2-chloro-1,3-butadiene.—A sample of 1-methyl-2-chloro-1,3-butadiene was exposed at room temperature to an ordinary incandescent light (150-watt Mazda) for one month. During this period the liquid increased in viscosity—slowly at first, but more rapidly later—until a soft, transparent, elastic, rubber-like solid was obtained. The rubber-like solid was macerated with alcohol to remove monomer and polymers of low molecular weight. The residual polymer was a tough, rubbery, plastic material. Ten per cent. by weight of zinc oxide was incorporated by means of steel rolls and the plastic mass then heated at 120° for twenty minutes. The product was strong, tough and elastic, but recovery from stretch was rather slow.

A sample of 1-methyl-2-chloro-1.3-butadiene was exposed to a 150-watt Mazda light at 30–35° for six and one-half weeks. The liquid progressively increased in viscosity until finally a pale yellow rubbery solid was obtained. This product was more completely polymerized than the product of the preceding experiment. The polymer was highly elastic and resembled cured natural rubber.

1-Ethyl-2-chloro-1,3-butadiene.—A sample of 1-ethyl-2-chloro-1,3-butadiene was exposed to the light of a 150-watt Mazda lamp at 30 to 35° for about four weeks. The product was a pale yellow, transparent, viscous sirup. This was macerated with a large volume of alcohol to remove unchanged monomer. The soft, sticky, coherent mass that remained undissolved by the alcohol was mixed with 10% of zinc oxide and heated in a mold for twenty minutes at 120°. The product was a tough, elastic material resembling the vulcanized product obtained from 1-methyl-2-chloro-1,3-butadiene, but it was softer and less resilient.

1-Butyl-2-chloro-1,3-butadiene.—A sample of 1-butyl-2-chloro-1,3-butadiene, when allowed to stand at the ordinary conditions in a stoppered bottle, after nine and one-half months had changed to a thick, sticky, brown sirup. Precipitation with alcohol then gave a 60% yield of rather soft, rubber-like material. The reaction was accelerated by light. A sample directly exposed to a 150-watt Mazda lamp at 30 to 35° for six weeks had changed to a yellow, viscous, sirup. After five weeks more it was considerably thicker. It was washed with alcohol and the residual sticky solid was mixed with zinc oxide. It vulcanized very incompletely on being heated.

A sample of 1-butyl-2-chloro-1,3-butadiene was subjected to a pressure of 6000 atmospheres at 38". At the end of ninety-six hours it had polymerized to a transparent, soft, sticky solid; 90% of this solid was now insoluble in alcohol. The portion insoluble in alcohol was mixed with 10% of its weight of zinc oxide, 2% of stearic acid, and 1% of benzidine and then heated at 120°. The physical properties of the product indicated that it was very incompletely vulcanized. It was elastic but rather weak and somewhat sticky.

1-Heptyl-2-chloro-1,3-butadiene.—A sample of this diene showed no apparent change in color or viscosity when allowed to stand at the ordinary conditions for nine months. Polymerization occurred slowly when a sample was exposed to Sight from a Mazda lamp at 30 to 35°. After three and one-half weeks the sample had changed to a colorless, transparent sirup. After six more weeks it had become thick and very viscous. It was finally washed with alcohol and attempts were made to vulcanize the insoluble polymer in the presence of zinc oxide. The product was soft and sticky.

A sample of 1-heptyl-2-chloro-1,3-butadiene was subjected to a pressure of 6000 atmospheres at 38°. At the end of ninety-six hours it had polymerized to a transparent, sticky, elastic mass. Only 4% of the material was soluble in alcohol. The alcohol-insoluble polymer was mixed with 10% of zinc oxide, 2% of stearic acid, and 1% of benzidine and heated at 120°. The product was a sticky solid possessing very slight elasticity.

Acknowledgment.—We are indebted to Dr. H. W. Starkweather for the experiments at high pressure.

Summary

Substituted chloroprenes of the formula $CH_2{=}CH{-}CCl{=}CH{-}R$ in which R is methyl, ethyl, n-butyl and n-heptyl are described. These compounds all polymerize much more slowly than chloroprene and the polymers, though rubber-like, are inferior in quality to polychloroprene. The methyl compound polymerizes most rapidly and yields the best polymer, but compared with polychloroprene the polymer is lacking in resilience.

Substituted anthraquinones derived from the substituted chloroprenes are described.

WILMINGTON, DELAWARE

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[CONTRIBUTION NO. 114 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. X. The Chlorination of the Hydrochlorides of Vinylacetylene

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

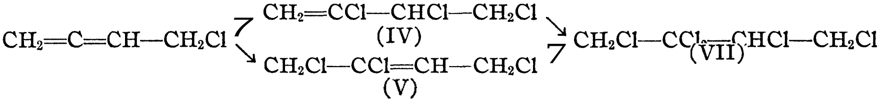
The action of hydrogen chloride on vinylacetylene gives rise to the two monohydrochlorides, chloro-4-butadiene-1,2 (I) and chloroprene (11), and the dihydrochloride, dichloro-2,4-butene-2 (III).[1]

$$CH{\equiv}C{-}CH{=}CH_2 \xrightarrow{HCl} \underset{(I)}{CH_2{=}C{=}CH{-}CH_2Cl} \longrightarrow$$

$$\underset{(II)}{CH_2{=}CCl{-}CH{=}CH_2} \xrightarrow{HCl} \underset{(III)}{CH_3{-}CCl{=}CH{-}CH_2Cl}$$

All of these compounds react rapidly with chlorine and we now record some observations on the products to which they lead.

Chloro-4-butadiene-1,2 in a series of experiments was chlorinated under various conditions and the combined distillable product was redistilled through an efficient column. Most of the material segregated into two fractions, one boiling at 40 to 41° at 10 mm. and the other at 64 to 65° at 10 mm. Each had the composition $C_4H_5Cl_3$. The lower boiling compound on oxidation with permanganate yielded α,β-dichloropropionic acid as the only recognizable product, and was thus identified as trichloro-1,2,3-butene-3 (IV). The higher boiling compound when similarly oxidized yielded only chloroacetic acid. The compound was therefore trichloro-1,3,4-butene-2 (V). The two compounds evidently arise by the addition of chlorine at the interior and the terminal members of the pair of contiguous double bonds. Other allenes have been observed to behave in a similar manner.[2]



$$CH_2{=}C{=}CH{-}CH_2Cl \begin{array}{c} \nearrow \\ \searrow \end{array} \begin{array}{c} \underset{(IV)}{CH_2{=}CCl{-}CHCl{-}CH_2Cl} \\ \underset{(V)}{CH_2Cl{-}CCl{=}CH{-}CH_2Cl} \end{array} \begin{array}{c} \searrow \\ \nearrow \end{array} \underset{(VII)}{CH_2Cl{-}CCl_2{-}CHCl{-}CH_2Cl}$$

Further experiments showed that although the two trichlorobutenes were the principal products when one mole of chlorine was added to chloro-4-butadiene-1,2, the ratio in which they were formed varied considerably with the conditions used. At 40 to 50° the 1,3,4-compound predominated, at −60 to −70° the 1,2,3-compound. Saturation of chloro-4-butadiene-1,2 with chlorine led to a compound having the composition $C_4H_5Cl_5$. In view of its origin it may be assigned the formula pentachloro-1,2,3,3,4-butane (VII).

In all of the chlorinations of chloro-4-butadiene-1,2 a considerable fraction (up to about 20% of the total product) consisted of undistillable ma-

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(1) Carothers, Berchet and Collins, THIS JOURNAL, 64, 4066 (1932).

(2) Bouis, *Ann. chim.*, [10] 9, 451 (1928).

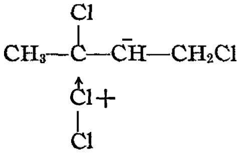
terial. In the chlorination of chloroprene (1 mole : 1 mole) the proportion of undistillable product was still greater (up to about 50%). The distillable product formed either at 40 to 50° or at -60 to $-70°$ was a difficultly separable mixture, but the principal fraction (25 to 30% of the total product) was closely similar in its physical properties to the compound already identified as trichloro-1,3,4-butene-2. This obviously might arise from chloroprene by a process of 1,4 addition.

The chlorination of dichloro-2,4-butene-2 leads to the formation of trichloro-1,2,3-butene-3 (IV), tetrachloro-1,2,3,3-butane (VI) and pentachloro-1,2,3,3,4-butane (VII). This series of products might be accounted for as follows

$$CH_3CCl{=}CH{-}CH_2Cl \xrightarrow{+Cl_2} \underset{\text{(VI)}}{CH_3{-}CCl_2{-}CHCl{-}CH_2Cl} \xrightarrow{-HCl}$$

$$\underset{\text{(IV)}}{CH_2{=}CCl{-}CHCl{-}CH_2Cl} \xrightarrow{+Cl_2} \underset{\text{(VII)}}{ClCH_2{-}CCl_2{-}CHCl{-}CH_2Cl}$$

The isolated tetrachlorobutane however is a stable compound, that is, it shows no tendency to lose hydrogen chloride spontaneously. Moreover, a very curious feature of the reaction lies in the fact that at elevated temperature (e. g., 40 to 60°) very little hydrogen chloride is evolved and the predominating product is the tetrachlorobutane; at low temperatures (e. g., -60 to $-70°$), on the other hand, hydrogen chloride is formed in copious amounts, and the predominating product is the trichlorobutene or the pentachlorobutane, depending upon the amount of chlorine applied. It appears therefore that the trichlorobutene does not originate from the tetrachlorobutane as such, but that both of these compounds arise from a common prior intermediate. Such an intermediate might be VIII, which would be formed by the addition of the chlorine molecule at the deficient carbon in the active form of the double bond.[3] Rearrangement of this intermediate would lead directly to tetrachlorobutane; loss of hydrogen chloride followed by rearrangement would lead to trichlorobutene. A sufficient difference in the temperature coefficients of the primary processes would account for the observed facts.



$$CH_3{-}\overset{\overset{Cl}{|}}{\underset{\underset{\underset{Cl}{|}}{\overset{\uparrow}{Cl^{+}}}}{C}}{-}\bar{C}H{-}CH_2Cl$$

(VIII)

The above statements in regard to the influence of temperature on the chlorination of dichloro-2,4-butene-2 are illustrated by the following experiments.

One mole (125 g.) of the dichlorobutene in a flask cooled with a slush of solid carbon dioxide and acetone was treated with chlorine gas until 1.33 moles of chlorine had been absorbed. The mixture was allowed to warm up while a slow stream of air was passed through it to remove dissolved

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(3) Carothers, THIS JOURNAL, 46, 2227 (1924). Evidence that chlorinations involve primarily attack by the chlorine molecule has been presented by Soper and Smith, *J. Chem. Soc.*, 1582 (1926).

gases. During this operation there was a sudden and very copious evolution of hydrogen chloride. The loss in weight corresponded with the evolution of 0.9 mole of hydrogen chloride. The hydrogen chloride collected and titrated was only 0.73 mole, but some was lost owing to the suddenness of the evolution. Distillation of the mixture gave

Trichloro-1,2,3-butene-3	0.440 mole
Tetrachloro-1,2,3,3-butane	0.089 mole
Pentachloro-1,2,3,3,4-butane	0.198 mole

The rest (0.273 mole) was contained in intermediate fractions and residue; the latter comprised 10.3% of the total product. If the losses are distributed proportionately among the three chief fractions, the percentage yields of these are

Trichlorobutene	60.6%	Tetrachlorobutane	12.2%	Pentachlorobutane	27.2%

Since in the formation of the pentachloro compound the trichloro compound is a necessary intermediate, 88% of the dichlorobutene was converted to the trichlorobutene, and only 12.2% to the tetrachlorobutane.

One mole (250 g.) of the dichlorobutene was chlorinated at ordinary temperature, the rate being controlled so that the temperature of the mixture was between 45 and 60°. The increase in weight corresponded with the absorption of 0.61 mole of chlorine, and at the same time 0.36 mole of hydrogen chloride was liberated. Distillation of the mixture gave

Trichloro-1,2,3-butene-3	0.207 mole
Tetrachloro-1,2,3,3-butane	0.343 mole
Pentachloro-1,2,3,3,4-butane	0.100 mole

Chlorination in this case was incomplete and there was considerable loss in residue and intermediate fractions, but the data show that the yield of tetrachlorobutane was greater than the combined yields of the trichloro and the pentachloro compounds. Further experiments showed that by careful adjustment of the amount of chlorine applied at low temperatures the isolated yield of trichloro-1,2,3-butene-3 could be raised to 80%, while at high temperatures the yield did not exceed 25%.

Oxidation of **Trichloro-1,2,3-butene-3.**—Twenty grams of the compound was stirred with 200 cc. of water while 70 g. of potassium permanganate was added in portions. The alkaline solution was filtered, treated with sulfur dioxide, filtered, acidified and continuously extracted with ether for nine hours. Evaporation of the ethereal solution gave 8.5 g. of acidic oil which distilled at 125° at 25 mm. It was identified as α,β-dichloropropionic acid by its melting point (49–50°) and its neutralization equivalent (calcd., 143; found, 141.1).

Oxidation of **Trichloro-1,3,4-butene-2.**—Oxidation of this compound under the same conditions as those described above gave chloroacetic acid as the only product. It was identified by its melting point (63°), mixed melting point and neutralization equivalent (calcd., 94.5; found, 95.1).

TABLE I

CHLORINATION PRODUCTS

Structural formula	Name	B. p., °C.	Mm.	d_4^{20}	n_D^{20}	M_R Calcd.	M_R Found
IV	Trichloro-1,2,3-butene-3	40-41	10	1.3430	14944	34.78	34 72
V	Trichloro-1,3,4-butene-2	64-65	10	1.3843	1 5175	34.78	34 89
VI	Tetrachloro-1,2,3,3-butane	90 55-57	32 10	1.4204	1.4958	40.14	40.25
VII	Pentachloro-1,2,3,3,4-butane	85	10	1.5543	1.5157	45.01	44.77

		Anal.					
		Calcd.			Found		
	Empirical formula	C	H	Cl	C	H	Cl
IV	$C_4H_5Cl_3$	30.09	3.13	66.77	29.95	3.30	66.34
V	$C_4H_5Cl_3$	30.09	3.13	66.77	29.09	3.01	67.33
VI	$C_4H_6Cl_3$			72.40			71.83
VII	$C_4H_5Cl_5$	20.82	2.16	77.00	21.22	2.36	77.05

Summary

Chlorination of chloro-4-butadiene-1,2 gives mixtures of trichloro-1,2,3-butene-3 and trichloro-1,3,4-butene-2 which react further to produce pentachloro-1,2,3,3,4-butane. The chlorination of chloroprene (chloro-2-butadiene-1,3) gives considerable amounts of trichloro-1,3,4-butene-2. The chlorination of dichloro-2,4-butene-2 at 40 to 60° proceeds with little loss of hydrogen chloride, and the product formed in largest amount is tetrachloro-1,2,3,3-butane. At low temperatures (—60 to —70°) large amounts of hydrogen chloride are liberated during the chlorination, and the principal products are trichloro-1,2,3-butene-3 and pentachloro-1,2,3,3,4-butane.

WILMINGTON, DELAWARE

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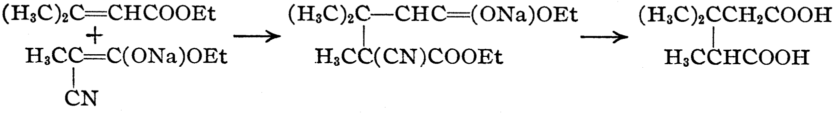
[CONTRIBUTION FROM CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Course of Addition of the Sodium Enolates of Malonic and Methylmalonic Esters to Benzalacetophenone and to Crotonic Ester

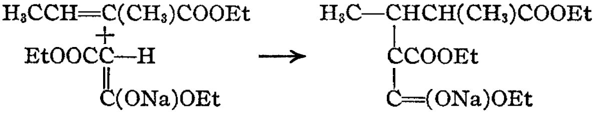
BY ARTHUR MICHAEL AND JOHN ROSS[1]

J. F. Thorpe[2] found that the addition product from sodium enol a-cyanopropionic ester and β,β-dimethylacrylic ester gave α,β,β-trimethylglutaric acid upon complete acid hydrolysis. From this result, he concluded that the methyl, not the sodium, of the addendum migrated in the reaction. This conclusion was not proved experimentally; the same glutaric derivative would be formed if the sodium had migrated to the α- A-carbon of the substituted acrylic ester, or to the A-oxygen of the adjacent carbethoxyl, with corresponding changes in the positions of unsaturation



$$\begin{array}{l}(H_3C)_2C{=}CHCOOEt\\ \quad + \\ H_3C\underset{\substack{|\\ CN}}{C}{=}C(ONa)OEt\end{array} \longrightarrow \begin{array}{l}(H_3C)_2C{-}CHC{=}(ONa)OEt\\ \qquad\ | \\ H_3CC(CN)COOEt\end{array} \longrightarrow \begin{array}{l}(H_3C)_2CCH_2COOH\\ \qquad\ | \\ H_3CCHCOOH\end{array}$$

With a normal course of addition, the free ester from the addition product of sodium enol methylmalonic ester and crotonic ester, and that formed by methylation of sodium enol α-carbethoxy-β-methylglutaric ester, should be identical. Examination of the reactions[3] showed that isomeric compounds are formed. This anomalous isomerism was explained by Michael and Ross[4] by the synthesis of the enolate of the first compound from sodium enol malonic and tiglic esters



$$\begin{array}{l}H_3CCH{=}C(CH_3)COOEt\\ \qquad\quad + \\ EtOOCC{-}H\\ \qquad\quad \| \\ \qquad\quad C(ONa)OEt\end{array} \longrightarrow \begin{array}{l}H_3C{-}CHCH(CH_3)COOEt\\ \qquad | \\ \qquad CCOOEt\\ \qquad | \\ \qquad C{=}(ONa)OEt\end{array} \qquad (A)$$

The synthesis of enolate **A** from sodium enol methylmalonic and crotonic esters could take place directly only by migration of the methyl of the former, but an isomer of A might be formed by that of its carbethoxyl, which might rearrange to A. It was concluded that the methyl shifted. Corresponding results were noted with analogous enolates and with other α,β, Δ-esters.[5]

Holden and Lapworth[6] have recently advanced a different interpretation of the course of the methylmalonic enolate–crotonic ester reaction. They assumed that Na— and $—C(CH_3)(COOEt)_2$ functioned as addendum

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(1) A preliminary communication appeared in THIS JOURNAL, **54**, 408 (1932).

(2) Thorpe, *J.* Chem. *Soc.*, **77**, 923 (1900).

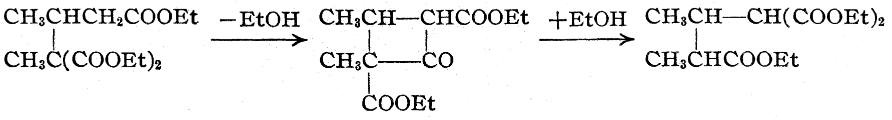
(3) Michael, *Ber.*, 33, 3731 (1900).

(4) Michael and Ross, THIS JOURNAL, **52**, 4598 (1930).

(5) Michael and Ross, *ibid.*, **53**, 1150 (1931).

(6) Holden and Lapworth, J. Chem. *Soc.*, 2368 (1931).

parts. Without implication of the sodium, they represented the course of reaction after the primary normal addition phase (I), as follows



$$\begin{array}{l}\text{CH}_3\text{CHCH}_2\text{COOEt}\\ \quad|\\ \text{CH}_3\text{C(COOEt)}_2\end{array} \xrightarrow{-\text{EtOH}} \begin{array}{l}\text{CH}_3\text{CH—CHCOOEt}\\ \quad\;|\qquad\;|\\ \text{CH}_3\text{C——CO}\\ \quad\;|\\ \quad\text{COOEt}\end{array} \xrightarrow{+\text{EtOH}} \begin{array}{l}\text{CH}_3\text{CH—CH(COOEt)}_2\\ \quad\;|\\ \text{CH}_3\text{CHCOOEt}\end{array}$$

I II III

Experiment and theory combine to make this view improbable. It had been shown that methylmalonic ester forms I when it reacts with crotonic ester in the presence of a little sodium ethoxide[7] and that I is also formed[8] by methylating the sodium enolate of β-methyl-γ-carbethoxyglutaric ester; further, on treatment with sodium ethoxide, that I undergoes almost quantitative fission into sodium enol methylmalonic and crotonic esters. Under these conditions, according to the interpretation of Holden and Lapworth, I should be converted into the sodium enolate of the tetracyclic ketone II and then into that of the open-chain ester III. The latter should undergo retrogression with sodium ethoxide to a considerable extent, with formation of tiglic not crotonic ester, but in the reaction in question the appearance of crotonic ester only was detected, nor was tiglic ester formed on refluxing I in ether solution with sodium ethoxide for several hours.

It has been shown experimentally, in agreement with the law of chemical neutralization, that such additions can take place only with degradation of free chemical energy. In these reactions, this is determined by the magnitude of neutralization of the positive chemical energy of the metallic atom of the enolate and, hence, addition is possible only when the energy of the metal is better neutralized in the addition product than in the original enolate. In the great majority of these reactions, the migration of the metal of the enolate would result in an increase of its free chemical energy. In agreement, it has been proved experimentally[9] that the hydrogen, not the sodium, of the —CONa—CH— group in the enolate migrates in such additions, provided a better neutralization of the metal is thereby obtained.[10]

Holden and Lapworth assumed that the metal of sodium enol methylmalonic ester united with the a-A-carbon of crotonic ester, or with the A-oxygen of the adjacent carbethoxyl, with positional rearrangement of unsaturation and the residual radical of the enolate united with the β-A-carbon to form IV. Intramolecular condensation of the Dieckmann type was now accepted and the reaction proceeded with elimination of

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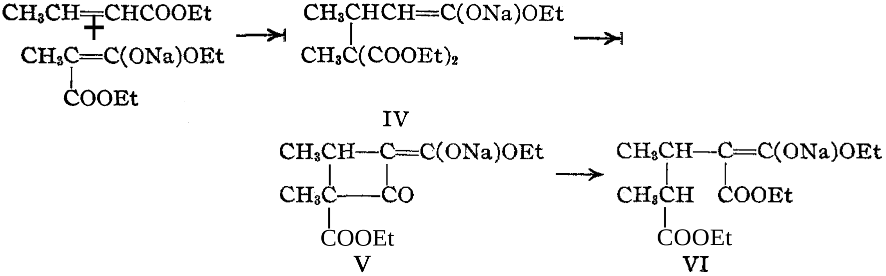
(7) Michael and Ross, THIS JOURNAL, 52, 4601 (1930).

(8) Michael, *ibid.*, 62, 3749 (1930).

(9) For literature on the subject, see Michael, *ibid.*, 62, 4599 (1930); 53, 1150 (1931).

(10) From the formation of α,γ-dimethyl-γ-cyanoglutaric ester upon methylation of the addition product from sodium enol cyanoacetic and a-methylacrylic esters, Thorpe[2] concluded that the a-hydrogen, not the sodium, of the enolate migrated in the reaction. The conclusion was not proved conclusively by the result of this experiment. If the sodium had migrated, an enolate of a monocarbethoxy group would have been formed, which would have rearranged spontaneously to the enolate of the cyanocarbethoxy group and this derivative would give the α,γ-dimethyl ester obtained by Thorpe.

alcohol to form the tetracyclic structure V, followed by addition of alcohol to form the open-chain enolate VI:



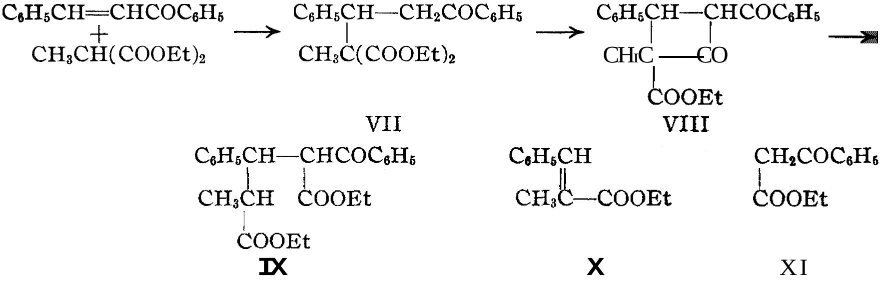
IV

V

VI

The intermediate production of IV would mean that the sodium would leave its original position in the enolate of the dicarboxylic ester group of methylmalonic ester to form the enolate of a monocarboxylic ester group. Such a change is impossible, since it would imply an increase in the chemical energy of the sodium and the addition could not proceed with degradation of chemical energy. Again, there is experimental evidence[11] that an enolate with the structure of IV would retrograde spontaneously into crotonic and sodium enol methylmalonic esters. In the conversion of IV to V, an intramolecular condensation to a tetracyclic derivative was assumed, although all attempts to realize a tetracyclic enolate synthesis have been without success. Further, V should rearrange mainly to the intramolecularly, better neutralized enolate, in which the sodium is located at the y-carbonyl group. This compound could not give VI by addition of alcohol, since the free chemical energy of the sodium would become thereby decidedly less neutralized. Even the conversion by alcohol addition of V to VI is theoretically improbable, since the free chemical energy of its sodium would become much less neutralized than in the stable enolate of V.

Holden and Lapworth support their interpretations by an examination of the reaction between sodium enol methylmalonic ester and benzalacetophenone (chalcone) in boiling benzene solution. Only products connected with retrogression, benzoylacetic (XI) and a-methylcinnamic (X) esters (45% of calcd.), were isolated. The reaction was expressed as



VII

VIII

IX

X

XI

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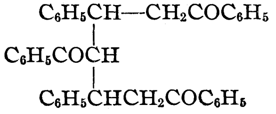
[11] Michael and Ross, THIS JOURNAL, 52, 4602 (1930).

It was considered that the sodium derivative of the normal addition product (VII) would be formed in the first instance and that there would then occur indirectly an exchange of a γ-COOEt for an a-hydrogen, yielding ester IX, with possibly the ketonic ester VIII as the intermediate step. The experimental results were regarded as conclusive evidence of an indirect exchange of position of a carbethoxy group of VII with an α-hydrogen and as demonstrating that the proof offered by Michael and Ross for the mechanism of the sodium enol methylmalonic–crotonic esters addition is "fallacious."

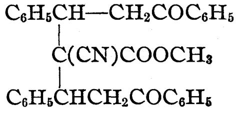
We have found that in the presence of piperidine, or of a small amount (0.1 mole) of sodium ethoxide, methylmalonic ester adds readily to chalcone to give approximately an 80% yield of VII, α-methyl-α-carbethoxy-β-phenyl-γ-benzoylbutyric ester. However, the action of sodium ethoxide (1 mole) or of metallic sodium (1 mole) on ester VII causes almost complete retrogression in the cold to give sodium enol methylmalonic ester (90%) and chalcone, perhaps with a trace of benzoylacetic ester, as the product gives a slight color reaction with ferric chloride. Evidently, this result is directly opposed to the interpretation of Holden and Lapworth, but agrees with our previous observations that enolates of compounds of the type of α,β-dimethyl-α-carbethoxyglutaric ester (I) undergo retrogression to the original additive components.

Holden and Lapworth have not taken into consideration the extraordinary tendency of chalcone to form addition compounds involving two of its molecules with one of an addendum. Kostanecki and Tambor[12] obtained compound XII by the addition of acetophenone to chalcone.



$$\begin{array}{l} \quad C_6H_5CH—CH_2COC_6H_5 \\ \qquad\;\; | \\ C_6H_5COCH \\ \qquad\;\; | \\ \quad C_6H_5CHCH_2COC_6H_5 \end{array}$$

XII



$$\begin{array}{l} C_6H_5CH—CH_2COC_6H_5 \\ \qquad\;\; | \\ \qquad C(CN)COOCH_3 \\ \qquad\;\; | \\ C_6H_5CHCH_2COC_6H_5 \end{array}$$

XIII

Kohler, Graustein and Merrill[13] found that it was difficult to prevent the formation of the "trimolecular" compound XIII in the addition of cyanoacetic methyl ester to chalcone, even when sodium ethoxide was used in small amount.

Dieckmann and Kron,[14] through the action of one mole of sodium enol malonic ester on two moles of chalcone, obtained a crystalline compound to which they assigned the hexacyclic structure XVIII.

α-Carbethoxy-β-phenyl-γ-benzoylbutyric ester (XIV), formed by the addition of malonic ester to chalcone,[15] may add to the latter in two ways, to give compounds XV and XVII, respectively. In the presence of sodium

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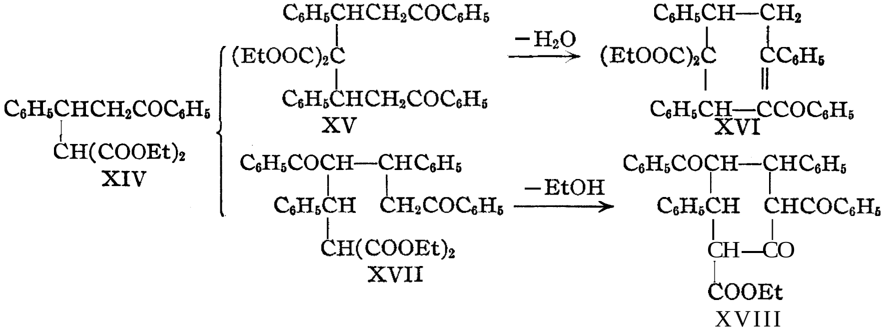
[12] Kostanecki and Tambor, Ber., 29, 1495 (1896).

[13] Kohler, Graustein and Merrill, THIS JOURNAL, 44, 2536 (1922)

[14] Dieckmann and Kron, Ber., 41, 1277 (1908).

[15] Kohler, Am. Chem. J., 46, 482 (1911).

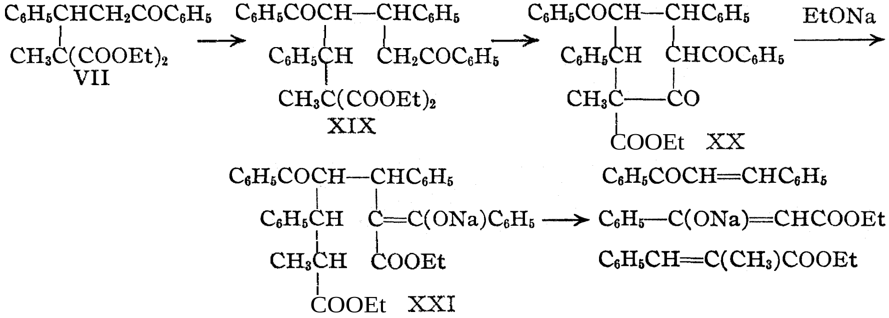
ethoxide, each of these may undergo condensation to a hexacyclic derivative; thus XV, by elimination of water, to give XVI, and the sodium enolate of XVII, to give the sodium enolate of XVIII by the elimination of alcohol:



We have reexamined the action of sodium enol malonic ester on chalcone and have found that the compounds XVI, XVIII and XVII can be readily obtained. The formation of XVI, 1,3,5-triphenyl-2-benzoyl-4,4-dicarbethoxycyclohexene-1, is favored by an excess of sodium ethoxide and the absence of alcohol. The enolate of XVIII, 1,5-diphenyl-2,6-dibenzoyl-4-carbethoxycyclohexanone-3, is formed in the action of chalcone on XIV in the presence of slightly less than one equivalent of sodium ethoxide. To obtain XVII strict attention must be paid to the purity of the reagents and to the concentration of the sodium ethoxide. This open-chain ester (XVII) is partially converted by sodium ethoxide into the enolate of the cyclic keto ester XVIII and, conversely, ester XVIII, upon treatment with sodium ethoxide, passes over to a very considerable extent into the sodium enolate of XVII. In these introconversion reactions, a small amount of the neutral, cyclic, compound XVI is also formed.

Ester VII can form only compound XIX with a second molecule of chalcone. In the presence of sodium ethoxide, this open-chain derivative may be expected to yield a mixture of the two possible enolates of the cyclic ketone XX. According to the results of Dieckmann[16] on the point of rupture between carbon atoms in analogously constituted enolates, ring-fission of the enolates of XX by alcohol should lead to enolate XXI, and this upon retrogression should give a mixture of chalcone, a-methyl cinnamic and sodium enol benzoylacetic esters. These are the products obtained by Holden and Lapworth from sodium enol methylmalonic ester and chalcone in boiling benzene solution. The intermediate cyclic enolate formed in this reaction must be an extremely labile substance, for, as stated below, practically the same amounts of the retrogression products are formed on standing of the mixture in cold ether as in boiling benzene. The above reactions are represented in the following scheme

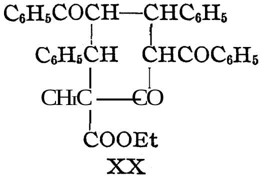
(16) Dieckmann, Ber., 33, 2670 (1900).

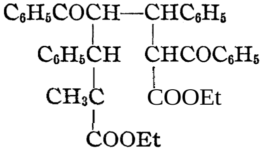

VII XIX XX XXI

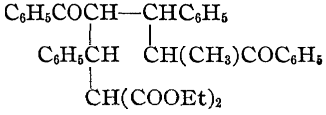
Attempts were made to prepare compounds XIX and XX, in order to examine their behavior toward sodium ethoxide. The products obtained by the action of sodium enol methylmalonic ester upon chalcone in cold ether solution were sodium enol benzoylacetic and a-methylcinnamic esters (50% approx.) and about 30% of a sirupy material of high molecular weight. From this sirup, a very small quantity of a crystalline solid was isolated which analyzed approximately for ester XIX, but it was obtained in too small an amount for further examination. Addition of chalcone to ester VII, using sodium ethoside, gave similar results and no increase of the supposed ester XIX. In the presence of piperidine, or of a small amount of sodium ethoxide, methylmalonic ester and two molecules of chalcone gave only the primary addition compound VII.

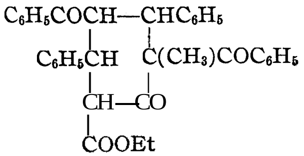
Resort was therefore made to the methylation of the sodium enolate of the cyclic derivative XVIII and that of the open-chain compound XVII. The latter can give only one enolate, involving the malonic ester group, and the former may give three enolates. However, as stated above, the enolates of the open-chain (XVII) and the cyclic (XVIII) compounds are intraconvertible and give a mixture in which that of XVII predominates. Evidently, XVII and XVIII should give the same products of methylation, which was confirmed by experiment. The reactions gave only a moderate yield of the methyl derivatives, probably due in part to polymerization of the mother substances. However, in accord with theory, the yield of the open-chain methyl derivatives was decidedly greater than that of the cyclic products.

Besides the cyclic 2- and 6-methyl derivatives (XX and XXIII, respectively), there were obtained the open-chain ε-methyl (XXII) and the α,ε-dimethyl (XXIV) products.

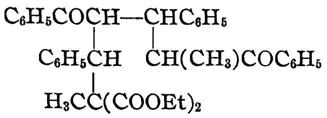

XX


XXI



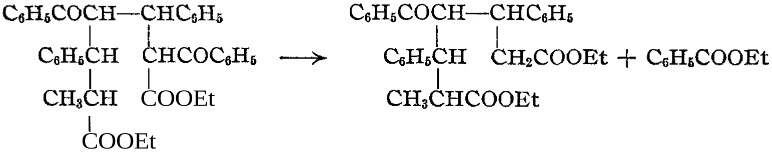


XXIII



XXIV

Upon addition to an ether–alcohol solution of sodium ethoxide, the cyclic 2-methyl keto ester (XX) dissolves immediately, with ring-fission by ethylate addition, to give the enolates of two apparently stereomeric[17] forms of XXI, and which upon warming in ether solution with ethylate undergo decomposition to form benzoic ester and α-methyl-β,β′-diphenyl-γ-benzoylpimelic ester (XXV)



XXI XXV

Upon treatment, in ether solution in the cold, with sodium ethoxide, the ester XXII was converted into an enolate of an isomer, and when heated in ether solution with sodium ethoxide it gave the sodium derivative of the cyclic ketone XXIII.

The structures attributed to the cyclic methyl derivatives XX and XXIII, and to the open-chain XXI and XXII, are based upon their behavior toward alcoholic ferric chloride. Ester XXII could enolize only at the malonic ester radical, but this group is always indifferent toward the reagent and the indifference of XXII conforms to the advanced structure. The cyclic XXIII contains the group RCOCHRCOOEt, which always shows the iron test and, accordingly, XXIII exhibits the. enolic reaction. Theoretically, XX, and the two isomers XXI, formed from XX by addition of alcohol, should be susceptible to the reagent, since

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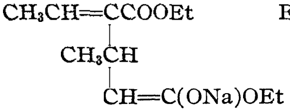
(17) The behavior of the isomeric esters XXIII and XX, and of XXII, toward sodium ethylate is without analogy in stereochemical reactions. No precedent is known for the conversion of XXII, before addition of alcohol, into the enolate of another form to yield finally the enolate of the cyclic XXIII; nor that XX should first give, by addition of ethylate, a mixture of the two open-chain enolates of XXI. It seems reasonable to suppose that XX, like XXIII, is converted into a mixture of its own and the enolate of a stereomer, and that the two stereomeric enolates of XXI are formed by addition of alcohol to the enolate mixture. It has recently been shown that an enolate may occur in stereomeric forms [Michael and Ross, THIS JOURNAL, 53,2401 (1931)].

Stereoisomerism is here used in the sense that certain organic compounds can find no expression in structural formulas and that the phenomenon in question is due to the spatial arrangements of the atoms in the molecules. This does not imply that the number and the configurations of the stereomers can always be coordinated with, or expressed in terms of, van't Hoff's views on spatial chemical isomerism. It has long been known that many organic isomers, stereomeric in the above sense, cannot be incorporated into the van't Hoff theoretical system, and that its space representations of the relations between saturated and unsaturated compounds are untenable. It is therefore difficult to understand that Lewis should have thought tenable spatial representations of the above relations from the octet viewpoint were obtained by changing from a conception of the carbon atom as a cube to that of a modified tetrahedron.—A. M.

they contain the enolizable $C_6H_5COCHRCO—$ group. It has been found, however, that certain compounds with similarly constituted groups, *i. e.*, $C_6H_5COCH(COOEt)CH(C_6H_5)CH_2COC_6H_5$, do not give the color test and structures assigned to XX and XXI therefore agree with their behavior toward ferric chloride.

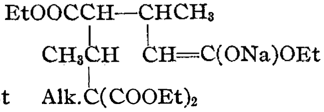
That ester XX upon treatment with sodium ethoxide should give benzoic ester and the pimelic ester derivative XXV, instead of the possible retrogression products, may be due to an unfavorable configuration of the primarily formed XXI. Similar to the behavior of XXII, this may undergo stereomerization and the product undergo decomposition instead of retrogression. It is also possible that the use of sodium ethoxide, instead of sodium enol methylmalonic ester, may be the determinative chemical factor. Clearly there is a qualitative difference in the reactivity of sodium ethoxide and sodium enol methylmalonic ester, but had the latter been used as the reagent, there would have resulted an ambiguity in the interpretation of the results. Although retrogression of ester XXI in the presence of sodium ethoxide could not be experimentally demonstrated, it must still be considered as a possible reaction by which benzoylacetic enolate and a-methylcinnamic esters could be produced in the reaction between sodium enol methylmalonic ester and chalcone.

It has been shown that crotonic ester under the influence of sodium ethylate,[18] or of metallic sodium,[19] is converted, with polymerization of two molecules of the ester, into the sodium derivative of α-ethylidene-β-methylglutaric ester (XXVI). In the reaction between sodium enol alkyl malonic and crotonic esters, a hexacyclic derivative might be formed by the union of alkyl malonic ester with enolate XXVII to form enolate XXVII, which with loss of alcohol might form the enolate of the hexacyclic XXVIII.



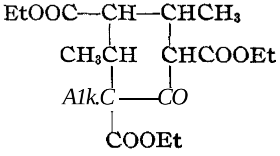
$$\begin{array}{l} CH_3CH{=}CCOOEt \\ \qquad\quad | \\ \quad CH_3CH \\ \qquad\quad | \\ \qquad CH{=}C(ONa)OEt \end{array}$$

XXVI



$$\begin{array}{ll} EtOOCCH & —CHCH_3 \\ \quad | & \quad | \\ CH_3CH & CH{=}C(ONa)OEt \\ \quad | & \\ Alk.C(COOEt)_2 & \end{array}$$

XXVII



XXVIII

In a previous paper,[20] it was shown that in the action of sodium enol ethylmalonic ester on crotonic ester a considerable quantity of XXVI, the enolate of the polymerization product of crotonic ester, and comparatively little of the addition product (XXVII, alk. = C_2H_5), appeared. However, with sodium enol methylmalonic ester none of enolate XXVI was formed, nor was it formed in the action of sodium enol α-cyanopropionic ester, although there was obtained in this reaction a very small

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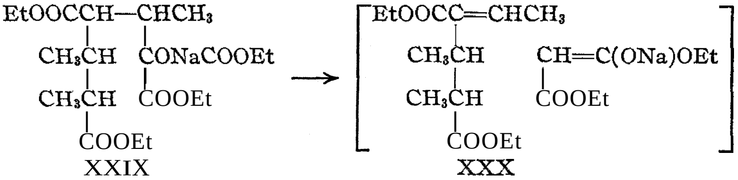
(18) V. Pechmann, *Ber.*, 33, 3340 (1900).

(19) Michael, *ibid.*, 33, 3760 (1900).

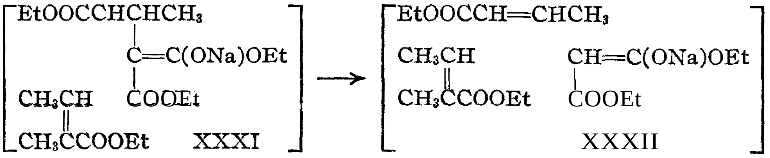
(20) Michael and Ross, This journal, 53, 1154 (1931).

amount of a keto ester, which may have had a hexacyclic structure corresponding to XXVIII.

Fission of ester XXVIII (alk. = CH_3) by alcoholic ethoxide should give primarily the enolate of the open-chain ester XXIX, which upon retrogression should give the products designated under XXX, XXXI or XXXII, or a mixture of these, namely, crotonic, tiglic, α-carbethoxy-β-methylglutaric esters and the enolates of malonic and α,β-dimethyl-γ-ethylideneglutaric esters.



$$\begin{array}{l} \text{EtOOCCH—CHCH}_3 \\ \quad | \qquad\quad | \\ \text{CH}_3\text{CH} \quad \text{CONaCOOEt} \\ \quad | \qquad\quad | \\ \text{CH}_3\text{CH} \quad \text{COOEt} \\ \quad | \\ \text{COOEt} \\ \text{XXIX} \end{array} \longrightarrow \left[\begin{array}{l} \text{EtOOCC}{=}\text{CHCH}_3 \\ \quad | \\ \text{CH}_3\text{CH} \qquad \text{CH}{=}\text{C(ONa)OEt} \\ \quad | \qquad\qquad\quad | \\ \text{CH}_3\text{CH} \qquad \text{COOEt} \\ \quad | \\ \text{COOEt} \end{array}\right] \\ \text{XXX}$$

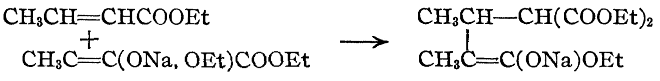


$$\left[\begin{array}{l} \text{EtOOCCHCHCH}_3 \\ \qquad\qquad | \\ \qquad\qquad \text{C}{=}\text{C(ONa)OEt} \\ \qquad\qquad | \\ \text{CH}_3\text{CH} \quad \text{COOEt} \\ \quad \| \\ \text{CH}_3\text{CCOOEt} \qquad \text{XXXI} \end{array}\right] \longrightarrow \left[\begin{array}{l} \text{EtOOCCH}{=}\text{CHCH}_3 \\ \text{CH}_3\text{CH} \qquad \text{CH}{=}\text{C(ONa)OEt} \\ \quad \| \qquad\qquad\quad | \\ \text{CH}_3\text{CCOOEt} \quad \text{COOEt} \\ \qquad\qquad\qquad \text{XXXII} \end{array}\right]$$

From these possible retrogression products the enolate of α,β-dimethyl-y-carbethoxyglutaric ester (B) could be formed only by the union of sodium enol malonic and tiglic esters. But it has been shown[20] that the ease of addition and the relative yield of the addition product is much smaller from sodium enol malonic ester and tiglic than from crotonic ester. Therefore, among the possible retrogression products, the enolate of malonic ester would add to crotonic ester in a much larger proportion than to tiglic ester, and the final retrogression products should be a mixture of tiglic with a relatively small amount of crotonic ester and the sodium enolates of β-methyl-α-carbethoxyglutaric and malonic esters.

Since the main product of the action of sodium enol methylmalonic ester on crotonic ester was enolate A, and no tiglic ester, the hexacyclic structure XXVIII cannot be considered as a possible intermediate in the formation of B from sodium enol methylmalonic and crotonic esters.

Besides through the migration of methyl, the formation of an enolate addition product may be considered as occurring by the direct migration of the carbethoxyl of sodium enol methylmalonic ester



$$\begin{array}{l} \text{CH}_3\text{CH}{=}\text{CHCOOEt} \\ \qquad + \\ \text{CH}_3\text{C}{=}\text{C(ONa, OEt)COOEt} \end{array} \longrightarrow \begin{array}{l} \text{CH}_3\text{CH—CH(COOEt)}_2 \\ \qquad | \\ \text{CH}_3\text{C}{=}\text{C(ONa)OEt} \end{array}$$

This interpretation seemed so improbable that it was not discussed previously. It implies the formation of a sodium enolate addition product in which the metal is less neutralized than in the employed enolate of methylmalonic ester. This course of migration would be contrary, therefore, to the law of chemical neutralization and it is also to our knowledge of the nature of such addition reactions.

In conclusion, the arguments advanced above may be summarized as follows. It has been shown that the formation of the cyclobutanone structurcs II and VIII of Holden and Lapworth is theoretically extremely improbable, and experimentally not possible with the use of such reagents as sodium ethoxide and sodium. Sodium enol benzoylacetic and a-methylcinnamic esters, as products of the action of sodium enol methylmalonic ester on chalcone, may be retrogression products of a hexacyclic enolate, formed by the union of two molecules of chalcone and one molecule of the methylmalonic ester enolate. It has been shown that hexacyclic structures are formed under the conditions of the reaction, but it has not been possible to complete experimentally the chain of steps intermediate to the formation of benzoylacetic enolate and α-methylcinnamic esters. However, it has been shown that the enolate of α,β-dimethyl-α-carbethoxyglutaric ester (B), obtained by addition of sodium enol methylmalonic to crotonic esters, could not have been formed through retrogression from a hexacyclic structure of a similar type.

Experimental

Addition of Malonic Ester to Benzalacetophenone.—α-Carbethoxy-β-phenyl-γ-benzoylbutyric ester was obtained as a solid melting at 71°, as described by Kohler,[15] by addition of malonic ester to one molecular equivalent of chalcone in ether solution. in the presence of a small amount of sodium ethoxide (0.1 mole), or a few drops of piperidine. The ester crystallized in fine needles from a mixture of ether and ligroin.[21]

α-Carbethoxy-β-phenyl-γ-benzoylbutyric acid was obtained from the above ester by saponification with alcoholic potash. Upon acidifying a sirupy product was obtained, which crystallized from an ether–ligroin mixture in fine needles, melting at 165° with decomposition.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.23; H, 5.57. Found: C, 69.05; H, 5.65.

From the mother liquor, or by slow crystallization, larger needle-like crystals were obtained, melting at 145°.[22]

Anal. Found: C, 69.12; H, 5.7.

The higher-melting acid was slowly converted into the lower-melting form upon standing in the air, or by slow recrystallization, but the higher-melting form was stable in a desiccator.

Action of One Mole of Sodium Enol Malonic Ester on Two Moles of Benzalacetophenone.—To a suspension of 1.2 g of pulverized sodium in ether, 8 g. of malonic ester was added. When the reaction was complete (twelve hours) a solution of 20.8 g. of chalcone in ether was added and then ether until the total volume was 300 cc. The mixture, cooled in ice water, was left for twenty-four hours, and an excess of acetic acid was slowly added with vigorous shaking. The ether solution was washed with

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[21] Barat [*J. Indian Chem. Soc.*, 7, 333 (1930)] described a compound, m. p. 150°, obtained by addition of malonic ester to benzalacetophenone, which upon saponification with caustic potash, gave an acid, m. p. 152–154°, and the latter when heated gave a "lactol," m. p. 158". The appearance of the compound of m. p. 150°, which Barat considered to be α-carbethoxy-β-phenyl-γ-benzoylbutyric ester (VII), we are unable to explain. In no experiment did we obtain a pure compound that would correspond to a substance of this melting point and analysis.

[22] Vorlander and Knotzsch [*Ann.*, 294, 332 (1897)] first obtained this acid.

aqueous sodium carbonate, then with water and the neutral solution dried and concentrated to about **100** cc. Cooling, or addition of ligroin, caused separation of crystals in the following order: very fine needles of the hexacyclic keto ester (XVI), m. p. **235"**; large hexagonal prisms of the hexacyclic keto ester (XVIII), m. p. 187°; large needles of the open-chain keto ester (XVII), m. p. 197°;[23] and, finally, fine needles of α-carbethoxy-β-phenyl-γ-benzoylbutyric ester (XIV), m. p. **71**°.

1,3,5-Triphenyl-2-benzoyl-4,4-dicarbethoxycyclohexene-(1) (XVI).—When two moles of sodium ethoxide are used with one mole of malonic ester and two moles of chalcone then the main product (70%) is ester XVI. Experiments indicated that the formation of this compound is favored by an excess of sodium ethoxide and prolonged time of reaction. It crystallizes from chloroform in fine needles, m. p. **235°**.

Anal. Calcd. for $C_{37}H_{34}O_5$: C, **79.57**; H, **6.09**. Found: C, **79.55**; H, **5.85**.

When warmed with alcoholic potash, it dissolved and after a few minutes a neutral. yellow oil was liberated. The aqueous extract when acidified gave α-carbethoxy-β-phenyl-γ-benzoylbutyric acid, m. p. 165°. The neutral, yellow oil, which did not crystallize, was probably a condensation, or a polymerized, product of chalcone

Addition of **Malonic** Ester to Two Moles of **Benzalacetophenone.**—A solution of **8** g. of malonic ester and **20.8** g. of chalcone in **200** cc. of ether was added to a sodium ethoxide solution from **0.2** g sodium in 4 cc. of alcohol and the mixture allowed to stand at room temperature for six weeks. Upon examination it was found that 0.5 g. of the hexacyclic keto ester XVIII and **17** g. of ester XIV were formed.

1,5-Diphenyl-2,6-dibenzoyl-4-carbethoxycyclohexanone-3 (XVIII).—After preliminary experiments, the following conditions were found to give the best yield: **0.5** g. of sodium was dissolved in 8 cc. of absolute alcohol and **100** cc. of dry ether added, when solution was complete. A solution of 104 g. of chalcone and 40 g. of malonic ester in **500** cc. of dry ether **was** then cooled to 0° and quickly added to the solution of sodium ethoxide. After a few minutes, it was necessary to cool the mixture in ice water and it then stood for twenty-four hours. **A** solution of **4.5** g. of sodium in **70** cc. of absolute alcohol was prepared, diluted with **100** cc. of ether and cooled to 0°. To this solution the above mixture was added with stirring and, after diluting with ether to one liter, the mixture was left to react for twenty-four hours.

The solution was acidified with acetic acid, washed with water and the acid and neutral products separated by extracting with 10% sodium carbonate solution. After drying, the ether solution of the neutral products was reduced to one-half of its volume by distilling off ether. Upon standing (sometimes before concentrating) the cyclic ketonic ester XVIII separated as large highly refractive prisms. A further quantity was obtained by addition of petroleum ether to the mother liquor, but this second crop contained some of the open-chain ester XVII, m. p. 197°. The material in the mother liquor consisted of chalcone and ester XIV. By treatment with a further quantity of sodium ethoxide in the preceding manner (using less than one equivalent of sodium ethoxide) a further quantity of the hexacyclic keto ester XVIII was obtained.

Anal. Calcd. for $C_{35}H_{30}O_5$: C, **79.23**; H, 5.53. Found: C, **79.13**; H, **5.7**.

A solution of this compound in acetic ester was added to an equivalent of sodium ethoxide in alcoholic solution and the mixture allowed to stand at room temperature for four hours. The neutral product of reaction consisted mainly (60%) of α-carbethoxy-β,δ-diphenyl-γ,ε-dibenzoylcaproic ester (XVII), approximately **30%** of the unchanged cyclic ketonic ester and a small amount (10%) of ester XVI.

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[23] Dieckmann and Kron [*Ber.*, 41, 1277 (1908)] in this reaction obtained a 20–30% yield of a crystalline compound, which melted at 197° and analyzed for the cyclohexene derivative XVI. We found that the compound corresponding to this analysis had m. p. 235°; the ester melting at 197° gave figures on analysis in agreement with the open-chain structure XVII. Moreover, the conversion of XVII into XVIII confirms the structure we have ascribed to this ester.

α-Carbethoxy-β,δ-diphenyl-γ,ϵ-dibenzoylcaproic Ester (XVII) crystallizes from a mixture of ether and chloroform in long needles and melts at 197°. It gives no color with ferric chloride in alcoholic solution.

Anal. Calcd. for $C_{37}H_{36}O_6$: C, 77.10; H, 6.25. Found: C, 77.29; H, 6.1.

When treated in acetic ester solution with two equivalents of sodium ethoxide in the cold, it is almost entirely converted into the enolate of the hexacyclic ketonic ester XVIII.

Upon methylation of the sodium enolate of XVII in acetic ester solution with methyl iodide, the same products were formed as by methylation of the sodium enolate of the hexacyclic ketonic ester XVIII.

Methylation of **1,5-diphenyl-2,6-dibenzoyl-4-carbethoxycyclohexanone-3 (XVIII).**—To a solution of 0.9 g of sodium in 15 cc of absolute alcohol 21 g. of XVIII dissolved in 400 cc. absolute, cold acetic ester was added with stirring. After a few minutes, an excess of methyl iodide (40 cc.) was added and the mixture allowed to stand at room temperature for twelve hours. It was then heated on the water-bath for six hours, when the solution was neutral to litmus. After distilling off the excess of solvent and reagent, the solution was cooled, washed with dilute mineral acid, then with aqueous soda and dried. The last traces of acetic ester were removed by heating in a vacuum, with the distilling flask in a water-bath. The residual sirup was then taken up in ether and the following compounds in turn crystallized out

(a) Ester XVII, m. p. 197°, 3 g. (c) Ester XX, m. p. 170°, 1 g.
(b) Ester XXII, m. p. 237°, 2 g. (d) Ester XXIII, m. p. 210°, 1 g.

There were also obtained small amounts of esters XXV and XX and there remained a considerable amount of unresolved material as a sirupy mixture.

α-Carbethoxy-β,δ-diphenyl-γ,ϵ-dibenzoyl-ϵ-methylcaproic Ester **(XXII).—This** compound crystallizes from chloroform-ether solution in large rhombic prisms, melting at 237°. It gives no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.54; H, 6.36.

One gram of the ester was powdered and added to a solution of 0.05 g. of sodium in 2 cc. of alcohol and the mixture diluted with ether. On shaking for about five minutes all the ester dissolved to form a yellow solution from which separated a small amount of *a* solid sodium derivative. After standing overnight, the mixture was acidified and flat needles, melting at 192°, gradually separated. This compound gives no color with alcoholic ferric chloride and according to the analysis it is isomeric or stereomeric with the original ester.

Anal. Calcd. for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.05; H, 6.20.

1,5-Diphenyl-2-methyl-2,6-dibenzoyl-4-carbethoxycyclohexanone-3-one (XXIII).—One gram of ester XXII was powdered, added to a solution of 0.05 g. of sodium in 2 cc. of alcohol and the mixture diluted with ether. After twelve hours it was heated with a reflux condenser on a water-bath for six hours. After cooling and acidifying, there was obtained 0.7 g. of ester XXIII, melting at 175° and crystallizing as large needles from chloroform-ether solution. It gives a deep red color with alcoholic ferric chloride.

Anal. Calcd. for $C_{36}H_{32}O_5$: C, 79.41; H, 5.93. Found: C, 79.33; H, 6.0.

1,5-Diphenyl-2,6-dibenzoyl-4-methyl-4-carbethoxycyclohexanone-3 (XX).—This compound, formed in the methylation of the sodium enolate of XVIII, crystallizes in fine needles from a chloroform-ether mixture, melting at 170°. It gives no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{36}H_{32}O_5$: C, 79.41; H, 5.93. Found: C, 79.30; H. 5.90.

Two grams of ester XX was brought into a solution of 0.1 g. of sodium in 3 cc. of absolute alcohol and ether added. The ester dissolved immediately, forming a deep red solution. In an hour, a small amount of a solid sodium derivative separated. After twelve hours, the mixture was acidified and there was obtained 1.7 g. of a mixture of esters, which were separated by fractional crystallization into two products. One is an ester, melting at 188°, crystallizing in large regular cubes. Analysis agrees with the open-chain structure XIX. It gives no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.42; H, 6.24.

The other product is an ester, melting at 210°, crystallizing in fine needles or nodular groups of needles. It gives no color with alcoholic ferric chloride. It is apparently a stereomer of XIX.

Anal. Calcd. for $C_{38}H_{38}O_6$: C, 77.29; H, 6.44. Found: C, 77.25; H, 6.30.

Two grams of the cyclic ester XX was added to a solution of 0.1 g. of sodium in 3 cc. of absolute alcohol and dry ether added. The solution of the enolate was heated with a reflux condenser for six hours. After cooling, it was acidified, the solution washed with aqueous soda and dried. On standing a neutral compound gradually crystallized out. There was obtained 1.0 g. of ester XXV, which crystallized as fine needles from ether-chloroform and melted at 154°. It gave no color with ferric chloride in alcoholic solution.

Anal. Calcd. for $C_{31}H_{34}O_5$: C, 76.53; H, 7.0. Found: C, 76.60; H, 6.80.

From the mother liquor, upon vacuum distillation in an oil-bath heated to 150°, a small amount (0.1 g.) of benzoic ester was obtained, which was identified by conversion into benzoic acid. The residue, after removal of the benzoic ester, contained a mixture of the open-chain, stereomeric ester XXI.

From the soda extract, 0.3 g. of material was obtained consisting of benzoic acid. It was purified by sublimation and identified by a mixed melting point.

α-Carbethoxy-α,ε-dimethyl-β,δ-diphenyl-γ,ε-dibenzoylcaproic Ester **(XXIV)**.—This substance, melting at 210°, was obtained by methylation of the sodium enolate of XVIII. It crystallizes in flat needles or nodules and gives no color with ferric chloride.

Anal. Calcd. for $C_{39}H_{40}O_6$: C, 77.49; H, 6.62. Found: C, 77.37; H, 6.4.

It is not soluble in alcoholic sodium ethoxide and is acted upon only slowly by this reagent.

Addition of **Methylmalonic** Ester to **Benzalacetophenone.**—α-Carbethoxy-β-phenyl-y-benzoyl-a-methylbutyric ester (VII) is obtained by addition of methylmalonic ester to one molecular equivalent of chalcone in ether solution, in the presence of a small amount of sodium (0.1 mole), or of a few drops of piperidine. The yield is about 80%. It crystallizes in large needles from a mixture of ether and ligroin and melts at 95°.

Anal. Calcd. for $C_{23}H_{26}O_5$: C, 72.21; H, 6.86. Found: C, 72.05; H, 6.6.

Upon treatment, in ether solution, with phenylhydrazine, it gives a phenylhydrazone, crystallizing in needles and melting at 130°.

Anal. Calcd. for $C_{29}H_{34}O_4N_2$: C, 73.41; H, 7.17. Found: C, 73.20; H, 7.3.

Upon warming with alcoholic potash, a vigorous reaction occurred with liberation of a yellow oil. This consisted, probably, mainly of chalcone; methylmalonic acid was isolated after acidifying the alkaline solution.

A solution of 9.5 g. of the ester in dry ether was allowed to react in the cold with 0.6 g. of powdered sodium. After twenty-four hours, most of the sodium had dissolved with slow evolution of a gas. From the neutral product of the reaction there was obtained 3.5 g. of methylmalonic ester, b. p. 80–90° (5 mm.), and 5.0 g. of a sirup which could not be distilled without decomposition, nor could it be obtained in a crystalline form.

An ether solution of 9.5 g. of the ester was mixed with sodium ethoxide, prepared by Brühl's method from 0.6 g. of granulated sodium. After twenty-four hours the mixture was acidified. From the neutral product there was obtained 3.8 g. of methylmalonic ester, and 5.0 g. of a sirup which crystallized on long standing and proved to be chalcone.

In the above two experiments no isolable amount of benzoylacetic or a-methylcinnamic esters was obtained. After removal of the methylmalonic ester, the residual sirup gave a faint red coloration with alcoholic ferric chloride, which might have indicated the presence of a very little of a β-keto ester (benzoylacetic ester).

Addition of Methylmalonic Ester (1 Mole) to Benzalacetophenone (2 Moles).—8.7 grams of methylmalonic ester was added to a solution of 21 g. of chalcone in ether and the mixture united with a solution of 0.1 g. of sodium in 3 cc. of absolute alcohol. After twenty-one days the solution was acidified and the reaction product worked up. It was found to consist of a-methyl-a-carbethoxy-8-phenyl-y-benzoylbutyric ester (16 g.), methylmalonic ester (1.5 g.), chalcone (10 g.) and traces of benzoylacetic and cinnamic esters.

When piperidine was used instead of sodium ethoxide, the products were the butyric ester derivative and unchanged chalcone.

Addition of Sodium Enol Methylmalonic Ester to Benzalacetophenone.—8.7 grams of methylmalonic ester in ether solution was treated with 1.2 g. of pulverized sodium When the reaction was complete, a solution of 20.8 g. of chalcone in dry ether was added and the volume made up to 300 cc. by further addition of ether. The mixture, cooled in ice water, was left for twenty-four hours, and it was then acidified with acetic acid. The neutral part of the reaction product was heated in an oil-bath up to 150° in a vacuum, and the distillate fractionated. There were obtained 2.5 g. of methylmalonic ester, b. p. 75–90' (2 mm.), 7.5 g. of α-methylcinnamic and benzoylacetic esters, b. p. 120–140° (2 mm.). The residue, consisting mainly of chalcone with products of polymerization, was dissolved in ether and ligroin added. On standing, a small amount (0.5 g.) of a solid was obtained, which was separated by fractional crystallization from chloroform–ether into two compounds, melting approximately at 185° and 235°, respectively. Owing to the small amount a further examination was impossible.

Action of Benzalacetophenone on α-Methyl-α-carbethoxy-β-phenyl-γ-benzoylbutyric Ester in Presence of Sodium Ethoxide.—Sodium ethoxide, prepared by the method of Brühl from 1.2 g. of granulated sodium, was suspended in dry ether and an ether solution of 19.2 g. of the butyric ester derivative and 10.8 g. of chalcone added. The mixture stood in the cold for twenty-four hours. Upon working up, as in the preceding experiment, there were obtained 5 g. of methylmalonic ester, 3 g. of a mixture of a-methylcinnamic and benzoylacetic esters, b. p. 120–140° (2 mm.), 0.5 g. of unchanged butyric derivative and a sirupy residue consisting of chalcone and amorphous products.

Summary

1. The action of sodium enol malonic ester on benzalacetophenone has been investigated, and the conditions for the two modes of addition of the latter to α-carbethoxy-β-phenyl-γ-benzoylbutyric ester determined.

2. It has been shown that one molecule of sodium enol malonic ester reacts readily with two molecules of benzalacetophenone to form two hexacyclic derivatives.

3. The addition of methylmalonic ester, and of sodium enol methylmalonic ester, to benzalacetophenone has been examined, the mechanism of the latter reaction discussed and Holden and Lapworth's interpretation shown to be impossible.

4. Contrary to the assumption of Holden and Lapworth, the production of benzoylacetic enolate and a-methylcinnamic esters in the action of sodium enol methylmalonic ester on benzalacetophenone, has no theoretical connection with the formation of sodium enol **α,β-dimethyl-γ-carbethoxyglutaric** ester in the union of sodium enol methylmalonic and crotonic esters.

5. It has been shown that a-methyl-a-carbethoxy-8-phenyl-y-benzoylbutyric ester, and α-carbethoxy-α,β-dimethylglutaric ester, do not form cyclobutanone structures when treated with sodium ethoxide or sodium, but undergo almost complete retrogression. These esters, or their enolates, therefore, cannot be intermediates in the addition reactions discussed above and for this reason alone the interpretations of Holden and Lapworth are untenable.

6. Certain difficulties arising from the assumptions of Holden and Lapworth have been discussed and it has been shown that the only explanation of the formation of the enolate of **α,β-dimethyl-γ-carbethoxy**glutaric ester from sodium enol methylmalonic ester, consistent with experiment and theory, is the migration of methyl during the addition process.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Action of Bleaching Powder on Ketones and on Ethyl Acetoacetate

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

In contrast to the general familiarity of the reaction between acetone and bleaching powder, very little is known of the action of bleaching powder on other ketones. Three substances each containing a CH_3CO— group were selected for study, namely, ethyl methyl ketone, furfuralacetone and ethyl acetoacetate.

Ethyl methyl ketone was selected to see if the reaction would yield chloroform and calcium propionate or ethylidene chloride and calcium acetate. Only the first of these two possibilities was realized. This provides a convenient source of propionic acid. Furfuralacetone, similarly studied, was found to be an excellent starting material for furylacrylic acid. Since furfuralacetone is readily prepared from furfural and acetone this method for the synthesis of furylacrylic acid is preferable to the Perkin reaction[2] which employs furfural, acetic anhydride and potassium acetate as reagents.

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(1) Holder of a Quaker Oats Fellowship (1929–1930) administered through the Miner Laboratories, Chicago.

(2) Baeyer, Ber.. 10, 357 (1877).

The general equation for this type of synthesis is

$$2RCOCH_3 + 6CaOCl_2 \longrightarrow (RCOO)_2Ca + 3CaCl_2 + 2Ca(OH)_2 + 2CHCl_3$$

In the cases mentioned above, R represents C_2H_5— and C_4H_3O—CH═CH—. Ethyl acetoacetate was studied to see if the enolic methylene hydrogens were the ones substituted by chlorine, in which case dichloroacetic acid would be anticipated, or if the methyl group would be attacked, giving chloroform, as in the former cases. The product formed was dichloroacetic acid and not chloroform. Therefore, the intermediate product was $CH_3COCCl_2COOC_2H_5$ and not $CCl_3COCH_2COOC_2H_5$.

Study was also made of the oxidation of furfuralacetone by nitric acid. Oxalic acid and ammonium tetroxalate were identified in the reaction products. This resembles the observation of Newbury and Orndorff[3] that ammonium tetroxalate was in the products from acetone and dilute nitric acid.

Experimental Part

Ethyl Methyl Ketone.—Three hundred grams of commercial bleaching powder (24% available chlorine) was made into a paste with 750 cc. of water at 15°. The temperature of the water must be above 10°, otherwise too viscous a paste results. This mixture was put into a 3-liter flask which was equipped with a dropping funnel, mercury-sealed stirrer and condenser. Then 25 cc. of ethyl methyl ketone was gradually introduced with stirring, care being taken to avoid frothing over. The mixture became quite warm and 10 cc. of chloroform, a 45% yield, distilled. The index of refraction, n_D^{20}, of the distillate was 1.4452; n_D^{20} of chloroform, 1.4458; n_D^{20} of ethylidene chloride, 1.4165.

The residue in the flask was neutralized with nitric acid. Then more nitric acid was added to liberate the propionic acid, purposely adding less than the calculated amount to avoid subsequent extraction of nitric acid. Even with an excess, however, ether extracts but insignificant quantities of nitric acid from a dilute aqueous solution.

The acidified solution was made up to 2000 cc. with water. An aliquot portion of 500 cc. of this was extracted four times with ether for the organic acid and the extracts made up to 250 cc. Titration of an aliquot portion of 50 cc. of this ether solution with 0.2016 N alkali required 27.5 cc. This corresponds to a yield of 8.18 g. or 40.7% of the calculated amount of propionic acid.

The identity of propionic acid was confirmed by a Duclaux determination. For this purpose, a dilute solution of 110 cc. of the acid (in water) was distilled and ten 10-cc. distillates obtained therefrom. The cc. of 0.2016 *N* base to neutralize each in turn was: 7.72, 7.87, 7.51, 7.12, 6.57, 6.33, 5.79, 5.40, 5.26, 5.64. The ratio of each 10-cc. titration to the total 100 cc. value gave the series: 11.8, 23.9, 35.4, 46.4, 56.5, 66.3, 75.1, 83.4, 91.5, 100.0. These percentages practically coincide with the values obtained by Gillespie and Walters[4] for propionic acid. Acetic acid, in contrast, gives rise to a series beginning with 8 and continuing with approximate multiples of 8.

Furfuralacetone.—Furfuralacetone was prepared by the method of "Organic Syntheses."[5] In some experiments it was purified by vacuum distillation to separate it from

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(3) Newbury and Orndorff, Am. *Chem. J.*, 12, 517 (1890).

(4) Gillespie and Walters, THIS JOURNAL, 39, 2036 (1917).

(5) Leuck and Cejka, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 42.

admixed difurfuralacetone. The purified product was collected at 110–112° (10 mm.); yield, 59–60%. In other experiments this tedious purification step was omitted. However, to ensure the removal of unused acetone the crude product was heated on a steam-bath for some hours. For purposes of calculation, it was assumed that this "crude furfuralacetone" contained 60% of furfuralacetone.

Furylacrylic Acid from Pure **Furfuralacetone.**—The details of this oxidation were identical with those previously described for ethyl methyl ketone, except that no dropping funnel was used. These quantities were involved: 300 g. of bleaching powder, made into a paste with 750 cc. of water at 15–20"; 37 g. of solid furfuralacetone; yield of chloroform, 18 g. or 55.5%. The reaction, as before, was exothermic and no external heat was applied. The paste in the flask was filtered and the filtrate acidified. The furylacrylic acid which separated was collected upon a filter. The filtrate from this operation was stirred up with the bleaching powder cake, boiled and refiltered. This filtrate gave more furylacrylic acid upon acidification. By repeating these steps, most of the furylacrylic acid was obtained in four such extractions. The yield was 33.5 g. or 89.5% of a product that melted at 139°.

Furylacrylic Acid from "Crude **Furfuralacetone.**"—A larger run was made from the crude furfuralacetone mentioned above. A yield of 89.7% of furylacrylic acid was obtained on the basis of the furfuralacetone content. These quantities were taken: 1800 g. of bleaching powder (in 4.5 l. of water), 275 g. of crude furfuralacetone; yield of furylacrylic acid, 205 g. The assumption that none of the furylacrylic acid came from the difurfuralacetone in the crude ketone was justified since no furylacrylic acid was isolable in a test run with bleaching powder and difurfuralacetone.

Ethyl Acetoacetate.—The reaction between acetoacetic ester (52 g.) and bleaching powder (350 g. made into a paste with 1 liter of water) was exothermic but there was no odor of chloroform. The liquid was filtered after the heating effect had stopped and the filtrate was acidified and extracted with ether. The residue, after evaporating the ether, was a brown liquid with a strongly acid reaction and a sharp odor. The liquid was shown to be dichloroacetic acid by converting it into dichloroacetyl chloride with phosphorus trichloride and then treating it with aniline to produce dichloroacetanilide, m. p. 118°. The yield of the dichloroacetic acid was 31 g. or 60% of the calculated value.

Furfuralacetone and Nitric Acid.—Cold, concd. nitric acid reacted on furfuralacetone with almost explosive violence. The reaction was very vigorous even when the acid was diluted with an equal volume of water. Hence the tests were limited to 1–2 g. samples. In this case, after the oxides of nitrogen had been expelled, the solution was concentrated. On cooling, crystals of oxalic acid dihydrate, m. p. 100–101°, separated. It gave the characteristically insoluble calcium oxalate.

In other experiments, 50 cc. of nitric acid was diluted with 200 cc. of water and warmed. Then 2 g. of powdered furfuralacetone was added while stirring was maintained. The red-colored oxides of nitrogen appeared momentarily. Then more furfuralacetone was added in small portions just large enough to keep the reaction going, the heat being removed when the reaction would proceed alone. The red color developed by each addition was allowed to disappear before another portion was added. This was continued until 20 g. of furfuralacetone had been added. Then the solution was evaporated to a volume of 35 cc. Upon cooling, crystals separated. These were filtered off and recrystallized from hot water. The crystals melted with decomposition at 128–130" and weighed 3.5 g. The substance was shown to be ammonium tetroxalate by titration with standard alkali and with potassium permanganate. It contained nitrogen, furthermore. Hence it could not have been furoic acid or maleic acid which also melt in this range but this was confirmed by mixed melting point depressions and by non-reaction of the compound with bromine.

Summary

Ethyl methyl ketone and bleaching powder react to give propionic acid and chloroform. Furfuralacetone gives furylacrylic acid and chloroform. Difurfuralacetone does not react to produce furylacrylic acid. Ethyl acetoacetate gives rise to dichloroacetic acid but no chloroform.

Oxalic acid and ammonium tetroxalate are among the reaction products of dilute nitric acid on furfuralacetone.

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Stereochemistry of Diphenyls. XXX.[1] Preparation and Resolution of 2,2′-Diiodo-4,4′-dicarboxydiphenyl

BY N. E. SEARLE[2] AND ROGER ADAMS

In an earlier paper[3] in this series it was pointed out that on the basis of the studies already completed on 2,2′,6 and 2,2′,6,6′-substituted diphenyls, there appeared to be no reason why certain 2,2′-disubstituted diphenyls should not be resolved provided the groups were large enough. Moreover, the fact that a disubstituted dinaphthyl[4] was successfully resolved, although such a compound is not entirely comparable to the disubstituted diphenyls, does indicate the likelihood of the existence of resolvable 2,2′-disubstituted diphenyls.

On account of the size of the sulfonic acid group as roughly estimated from the x-ray data available, it was predicted that a 2,2′-disulfonic acid derivative of a diphenyl might be resolved. Diphenyl-2,2′-disulfonic acid and 4,4′-diaminodiphenyl-2,2′-disulfonic acid were prepared, but attempts to resolve them resulted in failure. In the same communication it was pointed out that possibly the 2,2′-dibromo and probably the 2,2′-disubstituted diiododiphenyl should be resolvable. By the system of calculation previously used, based on x-ray data and using a value of 2.20 Å. for the C–I distance,[5] the interference on each side of the molecule should be approximately 0.12 Å.

A diiodo compound has finally been obtained, namely, 2,2′-diiodo-4,4′-dicarboxydiphenyl (IV). It readily formed dialkaloidal salts from which

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(1) For paper XXIX see Patterson and Adams, THIS JOURNAL, **55**, 1069 (1933).

(2) Submitted as part of a thesis for the degree of Doctor of Philosophy at the University of Illinois.

(3) Stanley and Adams, THIS JOURNAL, 62,4471 (1930).

(4) Stanley, *ibid.*, **53**, 3104 (1931); Meisenheimer and Beisswenger, *Ber.*, 65, 32 (1932); Corbellini, *Atti. R. Accad. Lincei* (Rome), *Rend.*, [6] 13, 702 (1931).

(5) In a previous paper the aromatic internuclear distance C–I was calculated as 2.06–2 35 Å. [see Neuburger, *Z. Krist*, 80, 118 (1931)]. The iodine atom has been demonstrated to be a polarizable atom in that its electron shell is easily distorted so that an average of the two limiting values given above seems a satisfactory approximation.

the brucine was selected for study.

Upon crystallization from ethyl alcohol only one form of the salt could be isolated, the salt of the I-acid. It is apparent, then, that the same phenomenon was in hand as obtained in the case of 2'-carboxy-6'-nitro-2-methoxydiphenyl and its derivatives as reported by Yuan and Adams.[6] The salt of the d-acid during evaporation of the solvent was obviously mutarotating to the salt of the I-acid which separated from solution.

When the salt was prepared in methanol, however, a first fraction was obtained which consisted of the salt of the d-acid and the other fractions the salt of the *l*-acid. By modifying the procedure it was also possible to obtain from the same solution two different types of crystal clusters which could be separated by hand. One, the smaller in amount, proved to be the salt of the d-acid, the other, in larger amount, the salt of the I-acid.

From Table I it may be seen that, as in previous racemization and mutarotation experiments, the solvent has a marked effect. The sodium salt in water racemizes more slowly than the free acid in organic solvents.

Two interesting articles by Lesslie and Turner[7] have just appeared in which the diphenyl ester of the 4,4'-diaminodiphenyl-2,2'-disulfonic acid **(I)** and the diphenyl-2,2'-disulfonic acid (II)

TABLE I

2,2'-Diiodo-4,4'-dicarboxydiphenyl	Wt.^{a} in g.	Solvent at 25°	l	Rotations: Max. $[\alpha]_D$ by extp.	Time^b in min.	Initial α_D	Initial $[\alpha]_D$	Final α_D	Final $[\alpha]_D$	Av. K^d	Av. dev. of K	Half-life period in min.
Brucine salt of *l*-acid	0.2023	Chloroform	2	−2 .6	11	−0.63	−25 .2	−0.09	−3.33	0.0043	±0.0002	70.0
Brucine salt of *d*-acid	.1522	Chloroform	2	+24.5	6	+0.47	+3 .2	.00	0.00	.0042	± .0003	71.7
Brucine salt of *l*-acid	.1512	Dioxane	2	−5 .5	11	−1.0	−9 .5	− .52	5.8	.0027	± .0004	111.5
l-Acid	.1515	Dioxane	1	−4 .6	5	−0.48	−47 .5	.00	0.0	.0033	± .0002	91.3
d-Acid	.0614	Dioxane	1	+5 .5	6	+ .2	+[illegible] .3	.00	0.0	.0033	± .0003	91.3
l-Acid	.1529	Ethyl acetate	1	−41.7	8	− .41	−[illegible] .2	.00	0.0	.0024	± .0002	125.4
Na salt of *l*-acid	.0999	Water^c	1	−3 .3	7	− .25	−[illegible] .5	.00	0.0	.0021	± .0004	143.4

$$K = \frac{1}{t} \log \frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f} \quad \left[\text{Half-life period; } T = (1/K) \text{ [illegible] } 2\right]$$

^{a} Made up to 15 cc. ^{b} Counted from time of adding solvent. ^{c} 0.1N NaOH solution was used. ^{d} Average of six values. The brucine salt was insoluble in ethyl acetate. The free acid was insoluble in chloroform and glacial acetic [illegible] idation or dimer [illegible] temperature. The sodium salt was insoluble in absolute alcohol.

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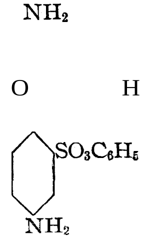
(6) Yuan and Adams, THIS JOURNAL, 54, 4434 (1932).

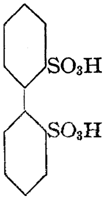
(7) Lesslie and Turner, J. Chem. Soc., 2021 (1932); *ibid.*, 2394 (1932).

have been resolved. It is obvious that the experimental work of Stanley and Adams in connection with the latter compound did not result in the discovery of the proper conditions for resolution. The successful resolution by Lesslie and Turner demonstrates the correctness of the prediction of Stanley and Adams that such disulfonic acids should be resolvable.

Turner has also described the preparation and resolution of another 2,2'-disubstituted diphenyl, the mono-methiodide of 2,2'-*bis*-dimethylaminodiphenyl (III).[8] Corbellini has prepared and resolved 2-(diphenylhydroxymethyl)-2'-carboxydiphenyl (IIIa).[8a] With the 2,2'-diiodo-4,4'-dicarboxydiphenyl (IV) described in this communication, five 2,2'-disubstituted diphenyls have been resolved and the possibility of the resolution of many others may be anticipated.



I



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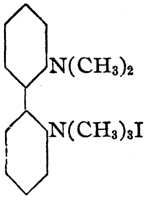

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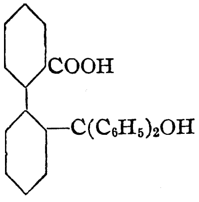
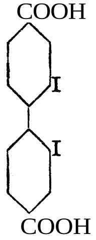


IIIa



IV

Lesslie and Turner[7] in their paper on the diphenyl ester of 4,4'-diaminodiphenyl-2,2'-disulfonic acid have discussed a procedure for estimating the resolution or non-resolution of substituted diphenyls. They have, at the same time, questioned the "theoretical justification" of the method for predicting resolvability or non-resolvability of such compounds, previously suggested by Stanley and Adams.[9] It may be stated merely that the assumptions made in connection with our calculations are fully recognized. On the basis of these calculations, predictions were made which conformed surprisingly well to the experimental results. The method of Lesslie and Turner is equally open to criticism since it involves arbitrary assumptions as to the effective diameter of certain atoms (*i. e.*, as to how close atoms can approach without interfering). The possibility of clarifying the diphenyl problem will depend primarily on the accumulation of additional pertinent experimental data.

Experimental

The 2,2'-diiodo-4,4'-dicarboxydiphenyl (IV) was prepared through the following series of reactions. (V) was condensed with copper to (VI), the nitro group reduced to (VII), diazotization to (VIII), rearrangement to (IX) and saponification to (IV).

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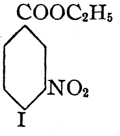
(8) Turner, *Nature*, 130, 315 (1932).

(8a) Carbellini and Pizzi, *Atti.* accad. *Lincei* **15**, 287 (1932).

(9) Stanley and Adams, THIS JOURNAL, **52**, 1200 (1930).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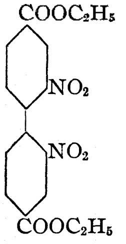
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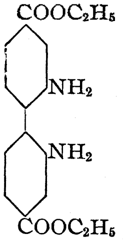
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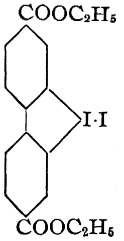
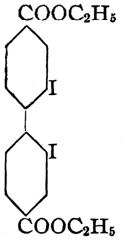
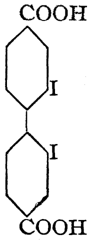

VIII


IX


IV

Ethyl **4-Iodobenzoate.**—A fine suspension of ethyl 4-aminobenzoate hydrochloride was prepared by adding 500 cc. of 6 *N* hydrochloric acid to 100 g. of ethyl 4-aminobenzoate, previously made into a thin paste with water. The suspension of the amine hydrochloride was cooled to zero degrees and diazotized with 48.2 g. of sodium nitrite dissolved in 100 cc. of water. During the diazotization about 100 g. of ice was added. To the diazotized solution, 160 g. of potassium iodide dissolved in 150 cc. of water was added with rapid stirring. On warming, a heavy black oil separated which was shaken with sodium bisulfite solution to remove excess iodine and distilled with superheated steam. The product was dried over anhydrous magnesium sulfate; yield, 122 g. (68.5% of theoretical); b. p., 281–283° at 760 mm.; 135° at 5 mm.; d^{20} 1.655; n^{25}_{D} 1.5854.

Anal. Calcd, for $C_9H_9O_2I$: C, 39.13; H, 3.26; I, 46.02. Found (micro): C, 39.63; H, 3.40; I, 46.28.

This product has been made previously by McCombie and Scarborough,[10] b. p. 153.5' at 14 mm., and by Schmidt and Schulz[11] by esterification of 4-iodobenzoic acid. .

Ethyl 3-Nitro-4-iodobenzoate (V).—A cold mixture of 60 cc. of concentrated nitric acid (sp. gr. 1.42) and 60 cc. of concentrated sulfuric acid was added slowly to a solution of 122 g. of ethyl 4-iodobenzoate in 150 cc. of concentrated sulfuric acid kept at 5–6° with ice and salt. This required one-half hour with good mechanical stirring and efficient cooling. Then the solution was allowed to warm up to 15° and was kept at that temperature until a yellow precipitate appeared (about two hours). The mixture was stirred for twenty minutes more and poured onto cracked ice. The ethyl 3-nitro-4-iodobenzoate separated as a yellow solid and was crystallized from 95% ethyl alcohol; yield, 120 g. of fine yellow crystals melting at 89–90.5°. The compound has been described previously by Allen,[12] who prepared it by esterification of 3-nitro-4-iodobenzoic acid. He reports a melting point of 88–89.5°.

2,2′-Dinitro-4,4′-dicarboethoxydiphenyl (VI).—A solution of 120 g. of (V) in 120 cc. of redistilled nitrobenzene was placed in a flask fitted with air-cooled condenser and mechanical stirrer and heated on a metal bath until the solution just began to boil. Then copper bronze powder was added slowly with stirring, causing the solution to boil more vigorously. When all further action had ceased, the nitrobenzene solution was filtered from the cuprous iodide and excess copper and was steam distilled. The residue was twice crystallized from 95% ethyl alcohol. The product consisted of pale yellow scales that melted at 95–96°; yield, 50 g. (69%).

Anal. Calcd. for $C_{18}H_{16}O_8N_2$: C, 55.68; H, 4.16; N, 7.22. Found (micro): C, 55.99; H, 4.24; N, 7.38.

2,2′-Diamino-4,4′-dicarboethoxydiphenyl (VII).—A solution of 15 g. of the dinitro

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(10) McCombie and Scarborough, J. *Chem. Soc.*, 107, 16 (1915).

(11) Schmidt and Schulz, Ann., 207, 334 (1881).

(12) Allen, *Bn.*, 26, 1742 (1893).

compound (II) in 350 cc. of 95% ethyl alcohol and 0.3 g. of platinum oxide[13] was reduced with hydrogen at a pressure of 35-45 lbs. The theoretical amount was absorbed in one-half hour. After several treatments with norite the diamine was precipitated by diluting the solution with water. It was recrystallized from dilute methanol and melted at 99–100°; yield from two runs, 20 g. of pale yellow scales (79%).

Anal. Calcd. for $C_{18}H_{20}O_4N_2$: N, 8.54. Found (micro Dumas): N, 8.57.

2,2′-Diiodo-4,4′-dicarboethoxydiphenyl (VIII) and (IX).—The procedure for replacing the two amino groups with iodine was similar to that used by Mascarelli and Benati[14] for converting 2,2′-diaminodiphenyl to the corresponding diiodo compound.

A suspension of 15 g. of (VII) in a mixture of 50 cc. of concentrated hydrochloric acid and 50 cc. of water was cooled with ice and salt and diazotized with 8 g. of sodium nitrite dissolved in 10 cc, of water. The cold diazonium salt solution was then filtered and a solution of 22 g. of sodium iodide in 50 cc. of water was slowly added with stirring. Upon warming the solution, a dark solid separated which was decolorized by adding sodium bisulfite. The product, 4,4′-dicarboethoxydiphenylene iodonium iodide (VIII), consisted of 20 g. of fine, light yellow powder that melted at 218° and was very insoluble in the usual organic solvents. It had the expected salt-like properties.[14]

Eighteen grams of (VIII) was heated at 218° for five minutes. After cooling, the dark product was taken up in 150 cc. of hot methyl alcohol and filtered. The filtrate was treated with decolorizing charcoal (norite) several times and the 2,2′-diiodo-4,4′-dicarboethoxydiphenyl (IX) was precipitated by adding water. After recrystallizing twice with dilute alcohol, 8 g. of white microscopic crystals was obtained melting at 118°.

Anal. Calcd. for $C_{18}H_{16}O_4I_2$: C, 39.30; H, 2.94. Found: C, 39.32; H, 3.21.

2,2′-Diiodo-4,4′-dicarboxydiphenyl (IV).—The ester was saponified by warming with alcoholic potassium hydroxide. The free acid was obtained by acidification with dilute hydrochloric acid and was recrystallized twice from dilute methanol. From 7.5 g. of ester, 5.5 g. of product was obtained as fine white crystals, m. p. 339–341°.

Anal. Calcd. for $C_{14}H_8O_4I_2$: neut. equiv., 247; C, 34.05; H, 1.63; I, 51.44. Found: neut. equiv., 249; C, 34.33; H, 1.74; I, 51.80.

Resolution of 2,2′-Diiodo-4,4′-dicarboxydiphenyl. (First Method)

Brucine Salt.—A solution of 3 g. of 2,2′-diiodo-4,4′-dicarboxydiphenyl in 140 cc. of absolute methanol was added to a solution of 4.8 g. of anhydrous brucine in 60 cc. of absolute methanol. After standing for one-half hour the salt came down as an oil. This was redissolved by adding 500 cc. more of absolute methanol and boiling. The solution was then evaporated to 450 cc. on the steam-cone. On standing overnight at room temperature 1.35 g. of salt precipitated as a fine powder, m. p. 212–224°. This fraction was dextrorotatory and was the salt of the d-acid (for rotations see Table I).

Anal. Less soluble salt—salt of d-acid. Calcd. for $C_{14}H_8O_4I_2 \cdot 2C_{23}H_{26}O_4N_2$: N, 4.37. Found (micro Dumas): N, 4.07.

The mother liquor from the first fraction was allowed to evaporate slowly at room temperature. After standing four days, a second fraction of 1.95 g. of salt crystals deposited. By allowing the mother liquor to evaporate spontaneously for a week at room temperature a third fraction of 2.90 g. of crystals was obtained. The second and third fractions were found to be identical in melting point and rotation and were different from the first fraction. They were levorotatory and proved to be the salt of *l*-acid, m. p. 201–212° (for rotations see Table I).

Anal. Calcd. for $C_{14}H_8O_4I_2 \cdot 2C_{23}H_{26}O_4N_2$: N, 4.37. Found (micro Dumas): N, 4.45.

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[13] "Organic Syntheses," Collective Vol. I, 1932, p. 452.

[14] Mascarelli and Benati, *Gazz. chim. ital.*, **38**, (II) 624 (1908).

(Second Method.)—Two moles of anhydrous brucine in ethyl acetate and one mole of racemic acid in ethyl acetate were mixed and allowed to stand overnight. The salt precipitated gradually and quantitatively. The mixture of the two diastereoisomeric salts was treated as follows.

A. A solution of **2.75** g. of the mixed salts in **250** cc. of ordinary methanol was allowed to evaporate slowly to **100 cc.** at room temperature. At first small hard hemispherical clusters of crystals formed but later clusters of larger, transparent prismatic crystals deposited. The mother liquor was poured off and the crystals washed with methanol. After drying, the two kinds of crystals were easily separated by hand. The hemispherical clusters that first appeared were in the smaller amount and were the salt of the d-acid. The prismatic crystals that formed later were in the larger amount and were the salt of the I-acid.

B. A solution of **4.3** g. of the salt obtained from the ethyl acetate process in 500 cc. of hot **95%** ethyl alcohol deposited **1.72** g. of crystals on cooling. After standing overnight **0.99** g. more of salt crystallized out. Upon evaporating at room temperature a third fraction of 0.84 g. was obtained. All three fractions were identical in melting point and rotation and were the salt of the I-acid.

_d_-2,2′-Diiodo-4,4′-dicarboxydiphenyl.—The d-salt was ground with ice-cold **6** *N* hydrochloric acid in a small porcelain mortar cooled by an ice-bath. The fine suspension thus produced was filtered on a sintered quartz filter and continuously washed with cold 6 N hydrochloric acid for four hours until the acid gave a negative test for brucine. After washing thoroughly with cold water it was dried *in vacuo* over sulfuric acid. From **0.65** g. of salt, **0.30** g. of active acid was obtained, m. p. 339–341° (for rotations and racemization see Table I).

_l_-2,2′-Diiodo-4,4′-dicarboxydiphenyl.—The 2-acid was obtained by the method used for the d-acid. From **3.0** g. of the I-salt, **1.1** g. of the active acid was obtained, m. p. **339–341°** (for rotations and racemization see Table I).

Summary

2,2′-Diiodo-4,4′-dicarboxydiphenyl has been prepared and resolved. The brucine salt mutarotates and the active acids readily racemize at 25°. The iodine and hydrogen atoms in the 2,2′-positions of diphenyl are of sufficient size to interfere with each other.

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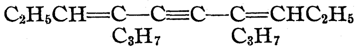
Reactions of Some Substituted Divinylacetylenes

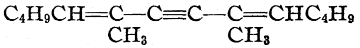
BY A. T. BLOMQUIST AND C. S. MARVEL

Although the behavior of the more complex conjugated unsaturated systems has been the subject of an increasing number of investigations during recent years, little attention has yet been given to the dienine system, $-C{=}C{-}C{\equiv}C{-}C{=}C-$. Vinylacetylene and divinylacetylene have recently been obtained by the polymerization of acetylene[1] and a few of their reactions have been described, but little is known concerning the higher members of this series of hydrocarbons. This communication describes a preliminary study of some of the addition reactions of two higher homologs of divinylacetylene.

Several years ago Dupont[2] described a general method of producing hydrocarbons of this type by the dehydration of acetylenic glycols. By this method, the two hydrocarbons, 4,7-di-*n*-propyldecadiene-3,7-ine-5 (I) and 6,9-dimethyltetradecadiene-5,9-ine-7 (11), were prepared through the glycols obtained from di-n-propyl ketone and methyl *n*-amyl ketone, respectively.


$C_2H_5CH{=}\underset{C_3H_7}{C}{-}C{\equiv}C{-}\underset{C_3H_7}{C}{=}CHC_2H_5$

I


$C_4H_9CH{=}\underset{CH_3}{C}{-}C{\equiv}C{-}\underset{CH_3}{C}{=}CHC_4H_9$

II

The first of these hydrocarbons was characterized by Dupont.[2] The second compound had not been previously prepared and it was necessary to establish its structure since there were two possible products of dehydration of the corresponding acetylenic glycol. Ozonization yielded n-valeric acid and pyruvic acid which proved that dehydration had occurred in the longer chain in accordance with the rule of Thorns and Ambrus[3] for the dehydration of unsymmetrical tertiary alcohols.

These substituted divinylacetylenes (I and II) were completely reduced by hydrogen in the presence of a platinum catalyst[4] to yield the corresponding branched chain paraffins, 4,7-di-*n*-propyldecane and 6,9-dimethyltetradecane. Some experiments in partial hydrogenation using two and four atoms of hydrogen per molecule of hydrocarbon produced complex mixtures of reduction products thus showing that under these conditions there is no preferential point of addition of hydrogen in this conjugated system. Bromination experiments also produced very complex mixtures of unstable compounds. Even at 0° the partially brominated hydrocarbons lost hydrogen bromide and changed into polymeric tars.

These substituted divinylacetylenes were more stable in air than the parent hydrocarbon, which has been found to polymerize and produce a

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(1) (a) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, 63, 4197 (1931); (b) Carothers, Williams, Collins and Kirby, *ibid.*, 63,4203 (1931).

(2) Dupont, Ann. *chim.*, [8] *30, 485* (1913).

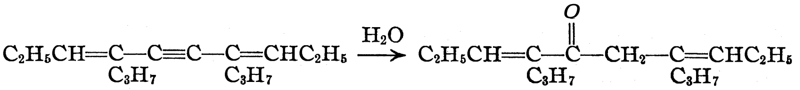
(3) Thoms and Ambrus, *Arch. Pharm.*, 263, 264 (1925).

(4) Adams and Shriner, "Organic Syntheses," Vol. VIII, 1928, p. 92.

hard film.[1a] The higher homologs did polymerize slowly when exposed in thin layers to the air but tack-free films were not obtained. Oxidation accompanied this polymerization as was shown by the fact that a measurable amount of oxygen was absorbed by a thin layer of 5,9-dimethyltetradecadiene-5,9-ine-7 (II). During this oxidation–polymerization the odor of the volatile fatty acids became apparent.

Maleic anhydride[5] added to this dienine system but the products obtained were amorphous compounds. No definite structure has as yet been determined for these addition products but analyses and titration values indicate that the ratio of unsaturated hydrocarbon to maleic anhydride is one molecule to two molecules.

The substituted divinylacetylenes were treated with sulfuric acid and acetic acid at about 25°, after the manner used by Grignard and Tchéoufaki[6] for the addition of water to conjugated diacetylenic hydrocarbons. In each case the compound produced had the empirical formula $C_{16}H_{28}O$, which showed that one molecule of water had added to the hydrocarbon. The product of this hydration reaction decolorized a solution of bromine in carbon tetrachloride and also aqueous potassium permanganate, indicating the presence of at least one unsaturated linkage. The presence of a carbonyl group was established by the formation of a 2,4-dinitrophenylhydrazone. The unsaturated ketone was not reduced by zinc and glacial acetic acid, which indicated that the olefinic linkage was not conjugated with the carbonyl group. This observation was surprising since the simple addition of water to the triple bond which was expected, would have led to a ketone with α,β- and β,γ-olefinic linkages (III). Further evidence to show that this simple addition of water was not the only reaction which had occurred was obtained by catalytic reduction of the hydration product to a saturated hydrocarbon, $C_{16}H_{32}$, rather than to the 4,7-di-*n*-propyldecane ($C_{16}H_{34}$) which had been prepared by the reduction of the original unsaturated hydrocarbon (I). A comparison of the physical constants of the hydrocarbon, $C_{16}H_{32}$, with those of 4,7-di-*n*-propyldecane showed about the same differences as are found between cyclohexane or its alkyl substitution products and the corresponding open chain paraffins.



$$C_2H_5CH{=}\underset{C_3H_7}{C}{-}C{\equiv}C{-}\underset{C_3H_7}{C}{=}CHC_2H_5 \xrightarrow{H_2O} C_2H_5CH{=}\underset{C_3H_7}{C}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\underset{C_3H_7}{C}{=}CHC_2H_5$$

I III

All of these data support the view that a carbon ring had formed during the hydration of the dienine. In a cyclization reaction the formation of a five or a six membered carbon ring would be predicted. A very reasonable mechanism to account for the formation of a six membered ring

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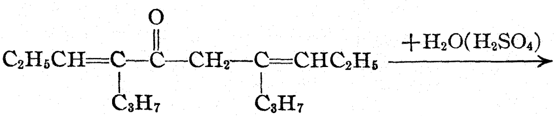
(5) The use of this reagent in the study of unsaturated conjugated systems was introduced by Diels and Alder, *Ann.*, 460, 98 (1928).

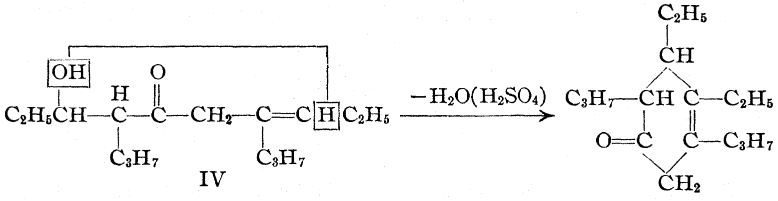
(6) Grignard and Tchéoufaki, *Compt.* rend., 188, 527 (1929); *Rec. trav. chim.*, 48, 899 (1929).

from the ketone (III) formed by the addition of water to the dienine is the following



$C_2H_5CH=\underset{C_3H_7}{C}-\overset{O}{\overset{\|}{C}}-CH_2-\underset{C_3H_7}{C}=CHC_2H_5 \xrightarrow{+H_2O(H_2SO_4)}$

III

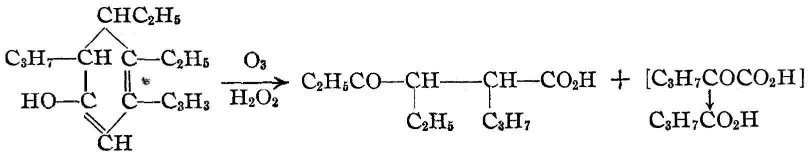


IV

V

The addition of a second molecule of water to the unsaturated ketone would undoubtedly occur as indicated at the α,β-unsaturation and ring closure of this type to give a six membered ring (V) is not unknown.[7]

The structure represented in formula V accounts satisfactorily for all of the reactions of the hydration product which have been mentioned above. Confirmation of this structure has been obtained by ozonization of the cyclic unsaturated ketone. This reaction produced n-butyric acid and a ketonic acid $C_{11}H_{20}O_3$ which did not have the ketonic group in the alpha or beta position with respect to the carbonyl group. Ozonization of the enol form of the unsaturated cyclic ketone (VI) would be expected to produce first α-ketovaleric acid and γ-keto-α-*n*-propyl-β-ethylcaproic acid (VII). This latter acid has the same empirical composition as the ketonic acid actually isolated from the ozonization. Under the conditions used in the decomposition of the ozonide, the α-ketovaleric acid would be expected to oxidize to n-butyric acid, which was actually isolated.



VI VII

Thus, all of the evidence indicates that a cyclohexenone derivative is formed by the action of sulfuric and acetic acids on the dienines.

In connection with this work on the dienines, an attempt was made to duplicate the preparation of a compound which was obtained by Dupont[2] by the dehydration of *sym*-tetra-*n*-propylbutinediol (VIII) and described as a five-membered ring containing a triple bond (IX). With other acetylenic

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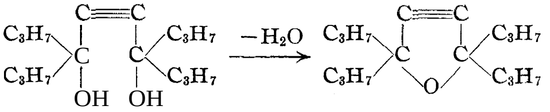
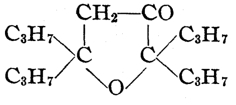
[7] **Reactions of this type have been observed in the terpene series, e. *g.*, the conversion of citral to cymene by the action of acetic and sulfuric acids which has been reported by Verley, *Bull. soc. chim.*, [3] 21, 408 (1899).**

glycols Dupont had obtained products which he described as tetrahydrofurans and only the tetrapropyl derivative gave this acetylenic cyclic compound.



VIII IX



X

When this reaction was repeated the product obtained agreed in properties and composition with the expected tetrahydroketofuran (X) and no substance corresponding to the acetylenic ring was isolated. This result shows that the tetrapropylacetylenic glycol is not exceptional in its behavior as Dupont has previously stated.

Some attempts were made to obtain the conjugated trienes corresponding to the substituted divinylacetylenes. It has previously been stated that partial catalytic reduction of the dienines has been found to be an unsatisfactory reaction because of the complex mixtures produced. Catalytic reduction of the acetylenic glycols to the olefinic glycols proceeded very smoothly but dehydration of the olefinic glycols gave only substituted dihydrofurans.

Experimental

Sym-tetra-*n*-propylbutine-diol.—This was prepared in yields of 72–73% as described by Dupont.[2]

Sym-dimethyl-di-*n*-amylbutine-diol.—Following the same general procedure this was prepared in 72–76% yields. The crude product consisted of a mixture of two stereoisomers; one (25 g.) melting at 86–87' after crystallization from petroleum ether (b. p. 65–110°) and the other (55–60 g.), a liquid which boiled at 144–146° (2 mm.). The solid isomer was analyzed.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.52; H, 11.89. Found: C, 76.76; H, 11.91.

Both glycols gave the same hydrocarbon on dehydration. A sample of the liquid isomer weighing 0.2931 g. liberated 48 cc. of ethane when treated with ethylmagnesium bromide; calcd., 50 cc.

4,7-Di-*n*-propyldecadiene-3,7-ine-5.—This was prepared by the method of Dupont.[2] *p*-Toluenesulfonic acid was less satisfactory than sulfuric acid as a dehydrating agent.

6,9-Dimethyltetradecadiene-5,9-ine-7.—This was prepared from 25 g. of the mixture of stereoisomers of sym-dimethyl-di-n-amylbutinediol by the action of sulfuric acid. The yield was 25 g.; b. p. 95–98" (0.5 mm.); n^{20}_D 1.4866; d^{20}_4 0.8241.

Anal. Calcd. for $C_{16}H_{26}$: C, 87.99; H, 12.01. Found: C, 87.10; H, 12.08.

Ozonization of **6,9-Dimethyltetradecadiene-5,9-ine-7.**—Ozonized oxygen was passed through a solution of 1.04 g. of the hydrocarbon in 200 cc. of carbon tetrachloride for about twelve hours. The solution of the ozonide was poured into about 40 cc. of 3%

hydrogen peroxide. The mixture was shaken vigorously and then the two layers were separated.

The aqueous layer was treated with phenylhydrazine and after two days the precipitate was filtered and recrystallized from alcohol. The product melted at 185–187° and the melting point was not depressed by mixing the material with an authentic specimen of pyruvic acid phenylhydrazone.

The carbon tetrachloride layer was extracted with 10% sodium hydroxide solution and the aqueous layer was separated. The organic acid was liberated with sulfuric acid, extracted with ether and converted to the p-bromophenacyl ester by the method of Judefind and Reid.[8] The ester melted at 61-62' and the melting point was not depressed when the ester was mixed with an authentic specimen of the *p*-bromophenacyl ester of n-valeric acid.

Reduction of 4,7-Di-*n*-propyldecadiene-3,7-ine-5.—To a solution of 10.02 g. of the hydrocarbon in 75 cc. of glacial acetic acid was added 0.2 g. of platinum oxide–platinum black.[4] The mixture was shaken under pressure with hydrogen until no more hydrogen was absorbed. The reduction gave 9 g. of 4,7-dipropyldecane, b. p. 92–93' (1.5 mm.); n_D^{20} 1.4368; d_4^{20} 0.7841. The physical properties differed slightly from those given by Dupont.[2]

Reduction of 6,9-Dimethyltetradecadiene-5,9-ine-7.—Ten grams of this hydrocarbon was reduced as described above. The hydrogen was absorbed very rapidly for two minutes and then insoluble material separated. After the addition of 125 cc. more of glacial acetic acid the reduction went to completion in about five minutes. The yield of 6,9-dimethyltetradecane was 9 g.; b. p. 103–104° (1.5 mm.); n_D^{20} 1.4348; d_4^{20} 0.7787.

Anal. Calcd. for $C_{16}H_{34}$: C, 84.88; H, 15.12. Found: C, 84.42; H, 15.31.

In other runs the reduction was interrupted after the addition of one and two moles of hydrogen. The reduction product was isolated and carefully fractionated. Various fractions were examined and some were ozonized in an attempt to establish structures. However, all indications were that the products were complex mixtures. Since it is unlikely that the identical mixture of products could be obtained in repeating these experiments no details are recorded here.

Addition of Bromine to the Substituted Divinylacetylenes.—Both of the divinylacetylenes added bromine rapidly when treated in chloroform solution with a solution of bromine in chloroform, but hydrogen bromide was evolved even at 0°. When the solvent was evaporated under reduced pressure at 0° only thick, viscous, greenish tars remained.

Drying Properties of the Substituted Divinylacetylenes.—About a half gram of each of the divinylacetylenes was dissolved in ether and the solution was evaporated on a watch glass to leave a thin film. In about twenty-four hours the film had considerable body but it never completely hardened. The compound with the methyl side chains appeared to dry the more rapidly. The rancid odor of the volatile fatty acids was noticeable after the second day.

A sample (0.0494 g.) of 6,9-dimethyltetradecadiene-5,9-ine-7 was placed on a filter paper and suspended in a flask of dry oxygen which was attached to a eudiometer filled with oxygen. During forty-eight hours this amount of hydrocarbon absorbed 4.54 cc. of oxygen (0°, 760 mm.). This corresponds roughly to one mole of oxygen for one mole of hydrocarbon. The absorption of oxygen was most rapid during the first four hours and was complete in forty-eight hours.

Addition of Maleic Anhydride to Substituted Divinylacetylenes. (a) 6,9-Dimethyltetradecadiene-5,9-ine-7.—A solution of 4.36 g. of the hydrocarbon and 1.96 g. of maleic anhydride in 25 cc. of anhydrous xylene was refluxed for about thirty hours.

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(8) Judefind and Reid, THIS JOURNAL, 42, 1043 (1920).

On cooling no solid separated, so the solution was refluxed for two hours with 10% sodium hydroxide solution. The aqueous layer was separated, filtered to remove suspended material, cooled to 10° and acidified with dilute hydrochloric acid. A yellow gummy acidic substance separated. This was collected in ether and the solution was washed thoroughly with water to remove maleic acid, dried over magnesium sulfate, filtered and concentrated to about **5–10** cc. On pouring this concentrated ether solution into **150** cc. of petroleum ether (b. p. **65–110")** a yellow amorphous powder separated. The precipitate was quickly collected on a suction filter and transferred to a vacuum desiccator. In this manner about **1** g. of a cream colored amorphous solid acid was obtained. The product was highly electrified. It did not possess a definite melting point when tested in a capillary tube, but slowly decomposed. On the Maquenne block it melted at 163°. It was insoluble in petroleum ether and benzene and soluble in ether, alcohol, acetic acid and acetone.

Analyses of various samples of this product gave carbon, 65.29–65.85% and hydrogen, **8 06–8 26%.** Titration gave a neutral equivalent of about **166.** However, when the sample was boiled with alkali this value fell to about **115.** This was taken to mean that the first product contained some anhydride groups which had not been previously hydrolyzed.

(b) 4,7-Di-*n*-propyldecadiene-3,7-ine-5.—The hydrocarbon gave results similar to those obtained in the preceding experiment. The product melted at 159° on the Maquenne block. It had a neutral equivalent of **149–153** and the values for carbon and hydrogen content were 64.85–65.09 and **7.47–7.70,** respectively. The neutral equivalent dropped to about **115** when the titration was carried out in a boiling solution.

Hydration and Cyclization of 4,7-Di-*n*-propyldecadiene-3,7-ine-5.—To a solution composed of **20** g. of concentrated sulfuric acid and **30** g. of glacial acetic acid was added **6** g. of the hydrocarbon. The temperature was held at room temperature (about 25°) and the mixture was stirred for about fifteen hours. The reaction mixture developed a deep red color during this time. The product was isolated by pouring the acid solution on cracked ice and extracting with ether. The ether solution was washed with 10% sodium carbonate solution and water and then dried over magnesium sulfate. After filtering the ether was evaporated and the residue was distilled under reduced pressure. The yield was **3** g. of a yellowish product, b. p. 107–110° **(0.7** mm.); n_{D}^{20} **1.4810;** d_4^{20} **0.8995.**

Anal. Calcd. for $C_{16}H_{28}O$: C, **81.29;** H, **11.95.** Found: C, **81.49;** H, **11.98.**

This product decolorized bromine in carbon tetrachloride and aqueous potassium permanganate. When treated with zinc in acetic acid solution some of the color was removed, but the compound was otherwise unchanged. The 2,4-dinitrophenylhydrazone[9] crystallized from alcohol in beautiful scarlet needles; m. p. **97–98".**

Anal.[10] Calcd. for $C_{22}H_{32}N_4O_4$: N, **13.44.** Found: **N, 13.44.**

The ketone could not be reduced with hydrogen and a platinum oxide–platinum black catalyst in alcohol but was reduced when glacial acetic acid was used as a solvent. To a solution of **3.44** g. of the ketone in 50 cc. of glacial acetic acid was added **0.2** g. of catalyst and the mixture treated with hydrogen under pressure. Absorption of hydrogen ceased in about eighteen hours. **A** second **3.04** g. of ketone was reduced and the two reduction mixtures were combined. The product obtained boiled at 97–100° **(1.5** mm.), n_{D}^{20} **1.4579;** d_4^{20} **0.8370;** M_{D} calcd. for $C_{16}H_{32}$ (cyclic) **73.92.** Calcd. for $C_{16}H_{34}$ (open chain) **76.12.** Found: **73.09.**

Anal. Calcd. for $C_{16}H_{34}$: C, **84.85;** H, **15.15.** Calcd. for $C_{16}H_{32}$: C, **85.61;** H, **14.38.** Found: C, 85.96; H, **14.44.**

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(9) Allen, THIS JOURNAL, **52**, 2955 (1930).

(10) This analysis was made by Mr. K Eder

The hydrocarbon was different from the 4,7-di-*n*-propyldecane obtained by the reduction of the original 4,7-di-*n*-propyldecadiene-3,7-ine-5 and was obviously a cyclic compound.

Ozonization of the Cyclic Ketone.--Ozonized oxygen was passed through a solution of 12 g. of the ketone in 150 cc. of carbon tetrachloride for about twelve hours. More solvent was added as needed to maintain the original volume. The ozonide was decomposed by shaking the solution with about 100 cc. of 3% hydrogen peroxide. The carbon tetrachloride solution was separated and washed with three successive 100-cc. portions of water. These washings were added to the hydrogen peroxide solution, made alkaline with sodium hydroxide and concentrated to about 100 cc. This solution was acidified with sirupy phosphoric acid and distilled until about 65 cc. of distillate was obtained. This distillate was exactly neutralized with sodium hydroxide and evaporated to dryness. The sodium salt was converted to the p-bromophenacyl ester[8] (3 g.) m. p. 62–63°. This melting point checks that of the p-bromophenacyl ester of n-butyric acid. A mixed melting point of the product with an authentic specimen of the n-butyric ester confirmed the identification.

The carbon tetrachloride layer remaining after the removal of the water-soluble material was extracted with 100 cc. of 5% sodium hydroxide solution. This alkaline solution was separated and acidified with hydrochloric acid. A sirupy acid separated and was collected in ether. After drying the ether solution over anhydrous magnesium sulfate and filtering, the ether was evaporated and the acid was distilled under reduced pressure, b. p. 110–112° (0.6–0.7 mm.). About 2 g. of this acid was obtained.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 66.00; H, 10.07; neutral equivalent, 200. Pound: C, 65.74; H, 10.02; neutral equivalent, 193.

A semicarbazone was prepared from 0.1 g. of this acid but the small quantity of available material prevented complete purification, m. p. 194–195°. However, the analysis indicated that the desired derivative had been obtained.

Anal.[10] Calcd. for $C_{12}H_{23}O_3N_3$: N, 16.35. Found: N, 15.56.

A neutral compound (about 3 *g.)* was obtained by evaporating the carbon tetrachloride solution which remained after the extraction of the keto acid. This material was a yellow oil which boiled at 82–88° (0.1 mm.); n^{20}_D 1.4710; d^{20}_4 1.043.

Anal.[10] Found: C, 61.05, 60.95; H, 8.39, 8.46. This compound was not further characterized.

Hydration and **Cyclization** of **6,9-Dimethyltetradecadiene-5,9-ine-7.**—Following the same procedure that was outlined above. 14 g. of this hydrocarbon gave 5.5 g. of an unsaturated ketone, b. p. 128–131° (1.5 mm.); n^{20}_D 1.4750; d^{20}_4 0.8958.

Anal. Calcd. for $C_{16}H_{28}O$: C, 81.29; H, 11.95. Found: C, 81.41; H, 12.01.

The 2,4-dinitrophenylhydrazone crystallized in beautiful carmine plates which melted at 104–105°.

Anal.[10] Calcd. for $C_{22}H_{32}N_4O_4$: N, 13.44. Found: N, 13.38.

Catalytic hydrogenation of the ketone in glacial acetic acid over a platinum catalyst gave a hydrocarbon; b. p. 101–103° (1.5 mm.); n^{20}_D 1.4533; d^{20}_4 0.8306.

Anal. Calcd. for $C_{16}H_{32}$: C, 85.64; H, 14.37. Found: C, 85.96; H, 14.47.

Hydration and Cyclization of **Sym-tetra-*n*-propylbutine-diol.**—A mixture of 10 g. of *sym*-tetra-*n*-propylbutine-diol and a solution of mercuric sulfate, which was prepared by dissolving as much mercuric oxide as possible in 100 cc. of water containing 5 cc. of concentrated sulfuric acid, was heated at 100° with stirring, under a reflux condenser for two days. The material was then steam distilled and the oil thus obtained was taken up in ether. After drying, the ether was removed and the residue distilled. About 5 g. of the tetrahydroketofuran was obtained; b. p. 96–100° (0.9 mm.); n^{20}_D 1.4608; d^{20}_4 0.9003.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.88. Found: C, 76.02; H, 12.05.

Hydration and Cyclization of **Sym-dimethyl-di-*n*-amylbutine-diol.**—The same procedure was used in this experiment as described for the propyl isomer. From 5 g. of the low melting isomer of the glycol there was obtained 3 g. of the substituted tetrahydroketofuran; b. p. 112–113° (1.0 mm.); n_D^{20} 1.4494; d_4^{20} 0.8977.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.88. Found: C, 75.15; H, 11.85.

Sym-tetrapropylbutene-diol.—A solution of 12.7 g. of *sym*-tetrapropylbutine-diol in 150 cc. of alcohol was reduced catalytically according to the method of Adams and Shriner[4] until one molecular equivalent of hydrogen had added. Eleven grams of a thick viscous colorless liquid was obtained. The olefinic glycol boiled at 136–138° (1.5 mm.).

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.57. Found: C, 74.72; H, 12.68.

Sym-dimethyl-di-*n*-amylbutene-diol.—Using the same procedure 12.71 g. of the low-melting isomer of sym-dimethyldi-n-amylbutine-diol gave 11.5 g. of the olefinic glycol; b. p. 128–130° (0.4 mm.); n_D^{20} 1.4657; d_4^{20} 0.9022.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.56. Found: C, 75.08; H, 12.43.

Similarly 12.7 g. of the pure high-melting isomer of the acetylenic glycol gave 11.8 g. of the olefinic glycol; b. p. 149-151"(2.0 mm.).

Anal.[10] Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.56. Found: C, 74.31; H, 12.59.

Dehydration of **Sym-tetrapropylbutene-diol.**—The same procedure was used in this dehydration as was described in the preparation of the substituted divinylacetylenes. From 10 g. of the butene-diol there was obtained 7 g. of 2,2,5,5-tetrapropyl-2,5-dihydrofuran, which was a colorless liquid; b. p. 92–94° (1.5 mm.); n_D^{20} 1.4635; d_4^{20} 0.8510.

Anal. Calcd. for $C_{16}H_{30}O$: C, 80.60; H, 12.64. Found: C, 80.78; H, 12.81.

Dehydration of **Sym-dimethyl-di-*n*-amylbutene-diol.**—From 10 g. of the olefinic glycol prepared from the low-melting acetylenic glycol there was obtained 7.6 g. of 2,5-dimethyl-2,5-di-*n*-amyl-2,5-dihydrofuran; b. p. 100–101° (3 mm.); n_D^{20} 1.4445.

Anal. Calcd. for $C_{16}H_{30}O$: C, 80.60; H, 12.69. Found: C, 80.77; H, 12.86.

Ten grams of the olefinic glycol obtained from the high-melting isomer of the acetylenic glycol yielded 7.5 g. of the same dihydrofuran derivative.

Summary

1. Two substituted divinylacetylenes, 4,7-di-*n*-propyldecadiene-3,7-ine-5, and 6,9-dimethyltetradecadiene-5,9-ine-7, have been prepared and their reactions with oxygen, bromine, hydrogen in the presence of a platinum catalyst and maleic anhydride have been investigated.

2. Treatment of these unsaturated hydrocarbons with a mixture of sulfuric and acetic acids has yielded cyclic unsaturated ketones which are apparently derivatives of cyclohexanone.

3. Some experiments on the dehydration and reduction of the intermediate acetylenic glycols have been performed and some di- and tetrahydrofuran derivatives have been described.

URBANA, ILLINOIS

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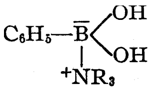
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Addition Compounds of Phenylboric Acid with Bases

BY DAVID L. YABROFF AND G. E. K. BRANCH

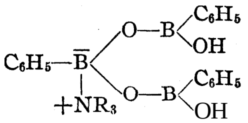
An addition compound of diethylamine and phenylboric acid was described in a brief communication.[1] There it was found that this compound contained three molecules of phenylboric acid to one of the amine. It was thought at first that loss of a molecule of water had occurred with the hydrogen of the amine and an hydroxyi group of the phenylboric acid, this being followed by addition of more phenylboric acid to the compound. It was pointed out that the analyses then obtained did not preclude the possibility of loss of a water molecule from the product. Since then we have investigated the action of other bases on phenylboric acid. The results obtained may be briefly summarized. (1) Addition compounds containing one mole of the amine and three moles of phenylboric acid are always obtained regardless of the nature (primary, secondary or tertiary) of the amine. (2) Bases as strong as pyridine will form stable compounds whereas weaker bases including aniline, nitriles, diphenylamine and acetic anhydride do not form stable addition products. (3) The percentage of carbon obtained for the diethyl and triethylamine compounds seems to indicate that two molecules of water have been eliminated from the product. Analyses of the propylamine compound are not self-consistent and seem to indicate the presence of an indefinite amount of water.

In view of results (1) and (3), the following mechanism appears probable



$$C_6H_5-\underset{{}^{+}NR_3}{\overline{B}}\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$$

"A"



"B"

A molecule of the amine combines with one of phenylboric acid yielding "A." The base strength of the hydroxyl oxygens is increased by the proximity of the negative charge on the boron atom, and combination with two more molecules of phenylboric acid occurs on the oxygen atoms. This is now stabilized by loss of two molecules of water, giving the stable product "B," which is actually isolated.

Experimental Section

Materials.—Phenylboric acid was prepared according to the method of Krause and Nitsche[2] by passing boron trifluoride into an ethereal solution of phenylmagnesium bromide. The boron trifluoride was prepared according to the method of Ruff[3] by heating a mixture of sulfuric acid, cryolite and boric oxide. The gas was passed through two freezing traps and through a tower containing a mixture of potassium fluoride and

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(1) Branch and Yabroff, THIS JOURNAL, **54**, 2569 (1932).

(2) Krause and Nitsche, *Ber.*, **55**, 1261 (1922).

(3) Ruff, "Die Chemie des Fluors," 1920, p. 25.

fused boric oxide before entering the Grignard solution. The amines were dried over solid potassium hydroxide and fractionally distilled.

Analyses.—Combustions were carried out in a tube containing two parts of copper oxide and one part of lead chromate in an atmosphere of air. A reduced copper spiral was placed at the end of the tube to reduce oxides of nitrogen. After most of the sample had been burned the tube was heated to redness in a stream of oxygen. The percentage carbon was always low, which was probably due to occlusion of charred particles by the boric oxide formed. The former method[1] used for the determination of nitrogen was found to give low results. Kjeldahl analyses which had been digested for twelve to twenty hours with 10 g. of potassium sulfate and 3 grams of potassium persulfate were found to give fairly good results even for the pyridine and piperidine compounds. Boron analyses were obtained by decomposing the compound by refluxing in alkaline solution, neutralizing to the methyl red end-point, and titrating with sodium hydroxide solution in the presence of glycerine with phenolphthalein as the indicator.

Procedure.—The amine (1 mole) and phenylboric acid (3 moles) were dissolved in dry ether. It was found that small amounts of water had no apparent effect on the reaction so no special precautions were taken to exclude moisture. Occasionally the addition product precipitated at once. Usually, however, part of the ether was evaporated and the mixture cooled in order to obtain precipitation. In certain cases petroleum ether was added and the solution evaporated to a very small volume. It was very difficult in certain cases to reproduce results once obtained. We varied the concentrations of the substances, tried the effect of small amounts of water and tried different temperatures, but were unable to determine the factors upon which the ease of precipitation of the compounds depended. The solid compounds obtained were washed with dry petroleum ether and evacuated for three hours. They were all stable in air. The propylamine compound did not precipitate so the ether was evaporated off and the residue recrystallized from hot kerosene, yielding a tan solid. Succeeding attempts always yielded an immediate white precipitate which varied in composition and melting point, so it was not investigated further. The compounds prepared and the analyses obtained are given in Table I.

TABLE I

	Amine	Color	M. P., °C.	Formula
1	Diethylamine	White	85	$(C_6H_5B(OH)_2)_3\cdot(C_2H_5)_2NH\cdot 2H_2O$
2	Triethylamine	White	39	$(C_6H_5B(OH)_2)_3\cdot(C_2H_5)_3N\cdot 2H_2O$
3	Propylamine	Tan	140–143	$(C_6H_5B(OH)_2)_3\cdot C_3H_7NH_2\cdot 2H_2O$
4	Pyridine	White	148–149	$(C_6H_5B(OH)_2)_3\cdot C_5H_5N\cdot 2H_2O$
5	Piperidine	Pink	213	$(C_6H_5B(OH)_2)_3\cdot C_5H_{11}N\cdot 2H_2O$

Petcentage composition

	Carbon		Hydrogen		Nitrogen		Boron	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	65.5	65.0 65.2	7.0	7.2 7.2	3.5	3.3 3.2	8.1	7.7 7.9
2	66.8	66.2 66.2	7.5	7.7 7.3	3.3	3.2 3.2	7.5	7.5 7.6 7.5
3	64.8	61.4 59.8	6.8	6.7 6.6	3.6	3.7 3.7		
4					3.4	3.2 3.3	7.9	7.8 8.0
5					3.4	3.2 2.8	7.8	7.8 7.5

Acetonitrile, benzonitrile, phenylacetonitrile, aniline, diphenylamine, acetic anhydride, acetylacetone and the sodium salt of acetylacetone failed to form stable addition compounds with phenylboric acid.

In conclusion we wish to express our thanks to Mr. A. C. Paiva, who kindly carried out the combustions.

Summary

Addition compounds containing three molecules of phenylboric acid and one of an amine with the elimination of two molecules of water have been described. Bases as strong as pyridine, but not nitriles, aniline or diphenylamine, form stable addition compounds. The structure of these compounds and a mechanism for their formation have been presented.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

The Preparation of 4-Fluoro- and 4,4′-Difluorobenzophenone

BY R. D. DUNLOP WITH JOHN H. GARDNER

In connection with an investigation in progress in this Laboratory it was desired to obtain some 4-fluoro- and 4,4′-difluorobenzophenone. The first of these has been previously prepared by Koopal through the condensation of *p*-fluorobenzoyl chloride with benzene,[1] but the second does not appear to have been prepared Since it has been shown that when phthalic anhydride is condensed with fluorobenzene by means of aluminum chloride the condensation takes place exclusively in the para position with respect to the fluorine atom,[2] it would be expected that the condensation with benzoyl chloride would take place in a similar manner.

As the first step in this investigation, it was shown that 4-fluorobenzophenone can be obtained through the condensation of benzoyl chloride with fluorobenzene, the product so prepared being identical with that resulting from Koopal's procedure, with no more than traces of the isomeric 2-fluorobenzophenone being formed. Similarly, the condensation of *p*-fluorobenzoyl chloride with fluorobenzene gave almost exclusively 4,4′-difluorobenzophenone. The product in this case was identified by subjecting its oxime to a Beckmann rearrangement, followed by hydrolysis to *p*-fluoroaniline and p-fluorobenzoic acid.

Experimental Part

4-Fluorobenzophenone.—A condensation of 18 g. of benzoyl chloride and 25 g. of fluorobenzene, using 20 g. of anhydrous aluminum chloride, working up the product in the usual way, gave 17 g. (66%) of colorless crystals, m. p. 48.2–48.7° from petroleum ether. A mixed melting point, using an authentic preparation made according to Koopal's method, m. p. 48.4–48.9 (Koopal gives 52°), demonstrated that both products were identical.

Anal. Calcd. for $C_{13}H_9OF$: F, 9.50. Found: F, 9.70, 9.64.

Evaporation of the mother liquors from the first two crystallizations gave less

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(1) Koopal, *Rec. trav. chim.*, *34*, 157 (1915); *Chem. Zentr.*, II, *332* (1915).

(2) Hahn and Reid, THIS JOURNAL, 46, 1645 (1924).

than 1 g. of a mixture of crystals and an oil which was not identified, showing that at most only a minute amount of 2-fluorobenzophenone had been formed.

4,4'-Difluorobenzophenone.—A similar procedure starting with 25.4 g. of *p*-fluorobenzoyl chloride, 35 g. of fluorobenzene and 30 g. of anhydrous aluminum chloride yielded 18.5 g. (52%) of colorless crystals, m. p. 107.5–108.5° from petroleum ether.

Anal. Calcd. for $C_{13}H_8OF_2$: F, 17.42. Found: F, 17.46, 17.35.

Evaporation of the mother liquor from the first crystallization gave about 1 g. of material melting at approximately 100°, indicating that only a very small amount at most of 4,2'-difluorobenzophenone had been formed.

4,4'-Difluorobenzophenoneoxime.—To a mixture of 5 g. of 4,4'-difluorobenzophenone, 3 g. of hydroxylamine hydrochloride, 6 cc. of water and 15 cc. of alcohol there was added in small quantities with shaking 5.5 g. of powdered sodium hydroxide. The mixture was boiled for five minutes and was then poured into a solution of 15 cc. of concd. hydrochloric acid in 100 cc. of water. The solid product was filtered off, dried and crystallized twice from toluene; m. p. 137–138°.

Rearrangement of 4,4'-Difluorobenzophenoneoxime.—To a solution of 2 g. of the oxime in 50 cc. of anhydrous ether there was added 5 g. of powdered phosphorus pentachloride. The ether was distilled off on the steam-bath and the residue was treated with 25 cc. of water. The product was filtered off, dried and recrystallized from alcohol, m. p. 183.5–184.2°.

Hydrolysis of ***p*-Fluorobenzo-*p*-fluoroanilide.**—One and one-half grams of the anilide was boiled with 200 cc. of constant boiling hydrochloric acid for six hours. An excess of 10% sodium hydroxide was added to the solution and it was distilled until the distillate no longer gave a precipitate with bromine water. About 0.5 g. of a light brown, oily liquid was extracted from the distillate with ether. On treatment with acetyl chloride, this gave a product melting at 150.8–151.3° after crystallization from water, in agreement with the value given by Holleman for the melting point of *p*-fluoroacetanilide.[3]

On acidifying the residue from the distillation with hydrochloric acid, there was obtained p-fluorobenzoic acid.

Summary

1. It has been shown that the condensation of benzoyl chloride and of *p*-fluorobenzoyl chloride with fluorobenzene takes place almost exclusively in the para position with respect to the fluorine atom.

2. 4,4'-Difluorobenzophenone has been prepared.

ST. LOUIS, MISSOURI

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[3] Holleman, *Rec. trav. chim.*, **25**, 330 (1906); Chem. *Zentr.*, II, 1830 (1906).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY WITH THE COÖPERATION OF THE RESEARCH DEPARTMENT OF THE ASSOCIATED MANUFACTURERS OF TOILET ARTICLES]

The Preparation of 5-Aminouracil and of Some of its Derivatives

BY MARSTON TAYLOR BOGERT AND DAVID DAVIDSON[1]

Requiring considerable quantities of 5-aminouracil in our studies of colored derivatives of uracil, we were led to attempt improvements in the existing methods of its preparation. 5-Aminouracil has generally been prepared by the reduction of 5-nitrouracil,[2] ferrous sulfate and ammonia being recommended for this purpose.

We have found technical sodium hydrosulfite to be a convenient reagent for effecting this reduction not only with 5-nitrouracil but also with its derivatives. 5-Nitrouracil itself may be obtained without previously isolating uracil by nitrating the reaction mixture obtained in the preparation of uracil according to Davidson and Baudisch.[3] In this way a considerable saving of time and of nitric acid is effected.

Sodium hydrosulfite is also useful in reducing the nitroso derivative of 6-aminouracil to 5,6-diaminouracil. In the experimental part is given a rapid modification of Traube's synthesis of this diamine.[4] Hepner and Frenkenberg[5] have also reported the use of sodium hydrosulfite in the reduction of a 5-nitroso-6-aminouracil derivative.

Experimental

Preparation of 5-Nitrouracil.—The hot reaction mixture obtained after heating the uracil reaction mixture for one hour according to Davidson and Baudisch[3] is stirred mechanically while 100 cc. of nitric acid (1.5) is slowly run in from a dropping funnel. The addition of the nitric acid causes a rise in temperature of the reaction mixture, which is allowed to proceed until the temperature reaches 105–110°. The flask may now be surrounded with water while the addition of nitric acid is continued, maintaining the inner temperature between 105–110°. It is important to maintain this temperature; otherwise nitric acid will accumulate in the reaction mixture and the reaction finally proceed with violence. When all the nitric acid has been added, the flask is heated on the steam-bath for one hour. It is then cooled and the contents poured into 1500 g. of ice. 5-Nitrouracil separates and is filtered off, washed with water and air dried; yield, 55–60 g. (47–51%). This product may be used without purification for the preparation of 5-aminouracil.

Preparation of 5-Aminouracil.—To a suspension of 15.7 g. of 5-nitrouracil in a solution of 10 cc. of concentrated ammonia in 250 cc. of water is added while stirring 75 g. of technical sodium hydrosulfite. The solution warms up, reaching 55° in ten to fifteen minutes. The mixture is finally heated to boiling, then cooled and filtered. The crude

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[1] A.M.T A. Research Department Fellow at Columbia University, 1931–1932.

[2] Johnson and Matsuo, THIS JOURNAL, 41, 782 (1919).

[3] Davidson and Baudisch, *ibid.*, 48, 2379 (1926): Johnson and Flint, *ibid.*, 53, 1079 (1931).

[4] Traube, *Ber.*, 33, 1371 (1900); Ann., 432, 266 (1923); Conrad, *ibid.*, 340, 310 (1905); Biltz and Schmidt, *ibid.*, 431, 94 (1923).

[5] Hepner and Frenkenberg, *Helv. Chim. Acta*, 16, 350 (1932).

product (10.0 g.) is dissolved in a mixture of 10 cc. of concentrated hydrochloric acid and 100 cc. of water. The solution is clarified with a bit of norite, diluted to 300 cc., heated to boiling, treated with 10 cc. of concentrated ammonia and cooled. 5-Aminouracil is obtained as colorless, silky needles; yield, 9.2 g. (73%).

Anal. Calcd. for $C_4H_5O_2N_3$: C, 37.8; H, 3.9. Found: C, 37.7; H, 3.9.

Preparation of Derivatives of **5-Aminouracil.**—When the procedure given above is applied to 5-nitro-6-methyluracil[6] and to 5-nitrouracil-6-potassium carboxylate[7] similar results are obtained.

Preparation of **5,6-Diaminouracil.**—To a solution of 4.6 g. of sodium in 75 cc. of absolute alcohol is added 6 g. of powdered urea and 11.3 g. (10.6 cc.) of ethyl cyanoacetate. The mixture is heated under reflux for two hours and then filtered hot. The sodium salt of 6-aminouracil thus obtained is washed with alcohol and air dried. It is then dissolved in 100 cc. of water, to which is added 50 g. of ice and 8 g. of sodium nitrite. This mixture is dropped into a mixture of 24 g. of acetic acid, 25 g. of water and 75 g. of ice. Concentrated ammonia is then added until the solution becomes ammoniacal, when the rose-colored salt of 5-nitroso-6-aminouracil is filtered off. This salt is then suspended in 250 cc. of hot water, 40 g of technical sodium hydrosulfite added, and the mixture heated to boiling while being stirred mechanically. The rose-colored salt is thus transformed into a buff-colored precipitate of 5,6-diaminouracil sulfate. The mixture is chilled and filtered. To purify the product, it is dissolved in 100 cc. of 6% sodium hydroxide containing a little sulfite, and the clarified solution poured into a boiling solution of 10 cc. of concentrated sulfuric acid in 100 cc. of water. After chilling, the 5,6-diaminouracil sulfate is filtered off, washed with water and air dried; yield, 13.0 g. (62%).

Anal. Calcd. for $(C_4H_6O_2N_4)_2H_2 \cdot SO_4$: C, 25.4; H, 3.6. Found: C, 25.3, H, 4.2. For analysis the product was dried at 120°.

Acknowledgment.—The authors are indebted to Mr. A. J. Flaxman for assistance in the study of the direct production of 5-nitrouracil.

Summary

Sodium hydrosulfite has been found to be a convenient reagent for the reduction of 5-nitro or nitroso derivatives of uracil to 5-amino derivatives.

NEW YORK, N. Y.
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(6) Behrend and Osten, Ann., 343, 133 (1905).

(7) Behrend. ibid., 240, 1 (1887); Biltz and Heyn, ibid., 413, 110 (1916).

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Catalytic Hydrogenation of Esters to Alcohols. III

BY HOMER ADKINS, BRUNO WOJCIK AND LLOYD W. COVERT

A limitation upon the catalytic hydrogenation of esters to alcohols[1] appeared to be the labilizing effect of carbinol, carbalkoxy and phenyl groups for the cleavage of the carbon to oxygen linkage in the alcohol.[2,3] For example, ethyl phenylacetate was hydrogenated to ethylbenzene as well as to β-phenylethyl alcohol, *i. e.*, $C_6H_5CH_2CO_2C_2H_5 \longrightarrow C_6H_5CH_2CH_2OH \longrightarrow C_6H_5C_2H_5 + H_2O$. It thus seemed desirable to direct attention toward modifications of the catalyst and of the conditions of hydrogenation which might minimize the hydrogenation of the carbalkoxy to a methyl group without decreasing the rate of conversion to a carbinol. This first objective has been sought in the further study of the hydrogenation of ethyl phenylacetate.

A comparison of catalysts and other factors in the hydrogenation of ethyl phenylacetate is a complicated matter because of the number of variables involved. At least five substances may sometimes be found in the product of hydrogenation, i. e., unchanged ethyl phenylacetate, phenylacetic acid, β-phenylethyl alcohol, ethylbenzene and the β-phenylethyl ester of phenylacetic acid. The alcohol and hydrocarbon are the result of hydrogenation, the ethyl phenylacetate of incomplete hydrogenation, the β-phenylethyl phenylacetate of alcoholysis, and the acid of hydrolysis. In addition to these reactions there may occur reduction of the catalyst from the black or active state to the red or relatively inactive state.

Folkers observed that the rate of hydrogenation, the proportion of products and the stability of the catalyst varied with different samples of ethyl phenylacetate. He was able to prepare from phenylacetyl chloride and ethanol samples of the ester which after careful fractionation could be hydrogenated rapidly and completely. In contrast to this was the observation that the ester obtained by the alcoholysis of benzyl cyanide (either from a commercial source or prepared in this Laboratory) was especially deleterious in its effect upon the catalyst.

It has now been found that pure ethyl phenylacetate may be readily prepared by heating the commercial product with catalytic nickel under hydrogen (3 hrs., 175°, 100 atm.) and then distilling the product. This process results in the elimination of any halogen or nitrogen containing impurities. The chief impurity is apparently benzyl cyanide which is eliminated in part as N-di-/?-phenylethylphenylacetamide, (C_6H_5CON-

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(1) Adkins and Folkers, THIS JOURNAL, 53, 1095 (1931).

(2) Folkers and Adkins, *ibid.*, 64, 1145 (1932).

(3) Connor and Adkins, *ibid.*, 55, 4678 (1933).

$(CH_2CH_2C_6H_5)_2)$.[4] Di-p-phenylethylamine was no doubt produced from the cyanide.[5] This compound then reacted with ethyl phenylacetate to give the substituted amide. Phenylacetamide was also formed, as would be expected, since ammonia as well as di-β-phenylethylamine is produced by the hydrogenation of benzyl cyanide. The amounts of the amides obtained indicated that the original sample of the ester contained approximately 1% of benzyl cyanide.

It is obvious that a complete study of the hydrogenation of ethyl phenylacetate would be so extensive as to be of doubtful value in consideration of the magnitude of the work involved. The present study was primarily devoted toward ascertaining whether the ratio of alcohol to hydrocarbon could be increased by modification of the copper–chromium oxide catalyst.[6] As a result of a long series of experiments which need not be described in detail, this question must be answered in the negative. It appears that the ratio of β-phenylethyl alcohol to ethylbenzene is dependent upon the completeness of hydrogenation of the ester. That is to say the more completely the ester is hydrogenated the lower the amount of β-phenylethyl alcohol in proportion to the amount of ethylbenzene. This result is exactly what one would expect if the ratio of products is dependent only upon the relative concentration of the ester and the alcohol in the mixture undergoing hydrogenation. It means that none of the modifications of the catalyst effected a preferential action upon the hydrogenation of the carbethoxy as compared with the carbinol group The best yields of β-phenylethyl alcohol from ethyl phenylacetate will thus be obtained if the hydrogenation is interrupted prior to the completion of the hydrogenation of the ester. In practice the best yields were obtained if the hydrogenations were stopped when there was 5 to 10% of residual ester. Under these circumstances the yields of alcohol were approximately 60% based upon the amount of ester submitted to hydrogenation, and the time of hydrogenation was less than an hour. Yields as high as 80% of alcohol based upon the amount of ester hydrogenated were obtained by interrupting the hydrogenation at earlier stages.

Many things have been shown to lower the optimum yields of alcohol referred to in the preceding paragraph: *i. e.*, a large amount of methanol (40%), or a small amount of cyanides, amines, ammonia, or acids in the reaction mixture; incomplete decomposition or washing of the catalyst resulting in the introduction of nitrogenous material into the reaction mixture; and deficiency in amount or activity of catalyst. All of these

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(4) M.p. 143.5°. Anal. Calcd. for $C_{23}H_{23}NO$: N, 4.25. Found: N, 4.17. The compound was hydrolyzed and the corresponding amine hydrochloride and acid identified by mixed melting point with authentic specimens. The substituted amide has recently been obtained in 50% of the theoretical yield by subjecting a mixture of benzyl cyanide and ethyl phenylacetate to the conditions used for the purification of the ester.

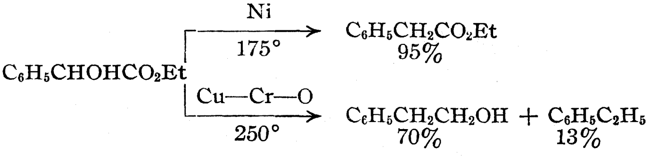
(5) *Cf.* Winans and Adkins, THIS JOURNAL, **54**, 307 (1932).

(6) Such a selective activation of nickel for the hydrogenation of benzyl alcohol and of furfural acetal has recently been described. Covert, Connor and Adkins, THIS JOURNAL, **54**, 1655 (1932).

changes in conditions of hydrogenation resulted in a lower ratio of alcohol to hydrocarbon, *i.* e., in a selective deactivation of the catalyst.

A second objective in this investigation was to increase the available information in regard to the effect of phenyl and cyclohexyl groups in various esters upon the ratio of products resulting from hydrogenation. To this end a number of esters containing one or the other of these groups were submitted to hydrogenation over copper–chromium oxide or nickel catalysts. A summary of the results is given below, the yields of various products being indicated.

Ethyl mandelate was hydrogenated to ethyl phenylacetate over nickel and over copper–chromium oxide to β-phenylethyl alcohol accompanied by some ethylbenzene. In the latter case the ratio of alcohol to hydrocarbon was higher than when ethyl phenylacetate was subjected to hydrogenation.

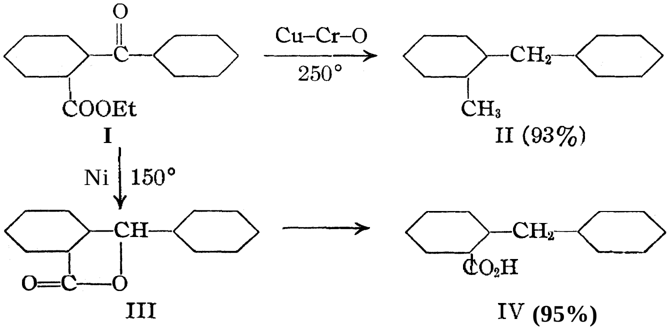


$$C_6H_5CHOHCO_2Et \begin{cases} \xrightarrow[175^\circ]{Ni} C_6H_5CH_2CO_2Et \ (95\%) \\ \xrightarrow[250^\circ]{Cu—Cr—O} C_6H_5CH_2CH_2OH \ (70\%) + C_6H_5C_2H_5 \ (13\%) \end{cases}$$

Ethyl phenylacetate was hydrogenated over nickel to ethyl cyclohexylacetate and this in turn over copper chromium oxide to β-cyclohexylethyl alcohol.

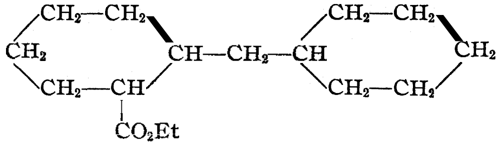
$$\underset{}{C_6H_5CH_2CO_2Et} \xrightarrow[200^\circ]{Ni} \underset{77\%}{C_6H_{11}CH_2CO_2Et} \xrightarrow[250^\circ]{Cu—Cr—O} \underset{94\%}{C_6H_{11}CH_2CH_2OH}$$

Ethyl o-benzoylbenzoate **(I)** was readily and almost quantitatively converted into either of two products depending upon the conditions adopted. (1) At 250° with the copper–chromium oxide catalyst the only product was *o*-benzyltoluene (II), the carboxyl having been converted into a methyl group.

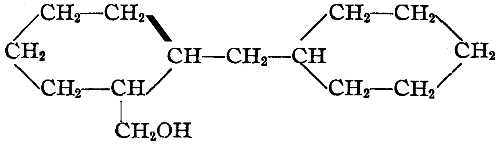


In alcohol, with nickel at 150° the ketone group was converted into a carbinol, the latter reacted with the carbethoxy group with the elimination of water and the formation of a lactone (III) which then underwent hydrogenolysis to o-benzylbenzoic acid (IV). The acid was not formed through hydrolysis, for the cleavage occurred quantitatively in an alcoholic solution under conditions in which hydrolysis of the ester would occur to a very small extent.

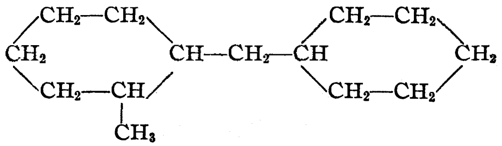
The ester of o-benzylbenzoic acid was smoothly hydrogenated over nickel at 150° to ethyl *o*-hexahydrobenzyl hexahydrobenzoate (V). This ester over copper–chromium oxide at 250° was hydrogenated to the corresponding carbinol (VI) accompanied by a small amount of the hydrocarbon (VII).



V (86%)



VI (74%)

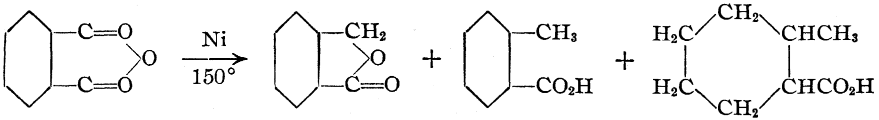


VII (8%)

The relative magnitudes of the effects of the phenyl group in the 1 and in the 4 positions with respect to a carbon to oxygen linkage is well illustrated by the ease and completeness of the hydrogenation of ethyl β-benzoylpropionate to 4-phenylbutanol-1.

$$C_6H_5COCH_2CH_2COC_2H_5 \xrightarrow[250°]{\text{Cu–Cr–O}} C_6H_5CH_2CH_2CH_2CH_2OH \ (94\%)$$

When phthalic anhydride was hydrogenated over nickel at 150° the first hydrogenation product was apparently phthalide (VIII).[7] There was also produced o-toluic acid (IX) and the corresponding hydrogenated compound, 2-methylhexahydrobenzoic acid (X).



VIII (34%) IX (36%) X (23%)

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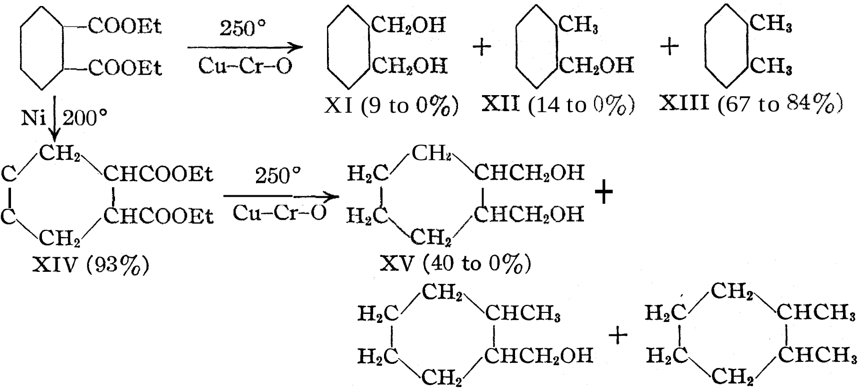
(7) *Cf.* Eykman, *Chem. Weekblad*, 4, 191 (1907).

The hydrogenation of diethyl phthalate over copper-chromium oxide catalyst gave a mixture of three products, i. e., phthalyl alcohol (XI), o-methylbenzyl alcohol (XII), and *o*-xylene (XIII). Over nickel the hydrogenation of diethyl phthalate proceeded smoothly to diethyl ha-hydrophthalate (XIV). This last ester, like diethyl phthalate, gave three products when subjected to the action of hydrogen in the presence of the copper-chromium oxide catalyst at 250°. These three compounds were the hexahydro derivatives of those obtained from diethyl phthalate (XV-XVII). However, it is important to note that while the hydrocarbon was the chief product from the phenyl ester, the glycol and alcohol were the chief products from the cyclohexyl ester.

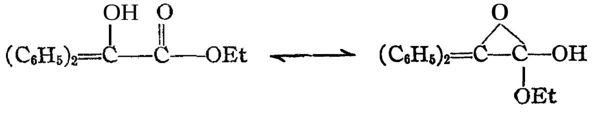


XI (9 to 0%) XII (14 to 0%) XIII (67 to 84%)

XIV (93%) XV (40 to 0%)

XVI (94 to 70%) XVII (6%)

The hydrogenation of benzilic ester gave unexpected results, for this ester was rather rapidly hydrogenated at 125°, a temperature about 100° lower than that required for other esters, and the glycol (1,1-diphenylethanediol-1,2) was obtained in a good yield (77%) despite the fact that one hydroxy group is but one carbon atom distant from a benzenoid ring, a position which renders it very labile toward hydrogenation. The low temperature required for the hydrogenation of the benzilic ester (XVIII) suggests that the hydrogenation proceeded through a tautomer (XIX), the hemiacetal of an oxido ketone (XIX).



XVIII XIX

Similarly ethyl diphenylacetate was rather rapidly hydrogenated at 200° (a temperature about 50° lower than for ethyl phenylacetate) with the formation of a fair yield (58%) of *β,β*-diphenylethyl alcohol, accompanied by 1,1-diphenylethane (38%). In the case of ethyl diphenylacetate it seems probable that the enol of the ester, $(C_6H_5)_2C{=}COHOEt$, is the compound undergoing hydrogenation. It has been shown by Staudinger and Meyer and by Cope and McElvain that this ester has so great a tendency to enolize that stable potassium and sodium derivatives of the enol may be obtained.[8]

The fact that the yields of alcohols previously obtained[2] by catalytic hydrogenation were 0% from ethyl benzoate, 97–100% from ethyl hexahydrobenzoate, 60% from ethyl phenylacetate and 93% from ethyl P-phenylpropionate, would lead to two tentative conclusions: **(a)** that a phenyl group in the 1 position with respect to a carbethoxy is completely effective, under the conditions for the hydrogenation of an ester, in labilizing the hydrogenolysis of a carbon to oxygen linkage, and progressively less so in the 2 and **3** positions; (b) that the hydrogenation of the benzenoid ring eliminates completely the effect noted in (a). The facts reported in this paper are in general those which might be expected on the basis of these tentative conclusions. However, certain of the results of the present work would not have been anticipated. For example, despite the fact that the carbethoxy groups in diethyl phthalate are adjacent to a benzenoid ring, phthalyl alcohol and o-methylbenzyl alcohol were obtained by hydrogenation. This result, in spite of the fact that the carbethoxy groups in diethyl phthalate are in the **3** position with respect to each other, as in diethyl succinate, a relationship which predisposes toward hydrogenolysis of the oxygen to carbon linkage.[2] Further, the temperature required for hydrogenation and the yield of glycols from ethyl benzilate and diphenylacetate are not at all those that would have been anticipated upon the basis of the behavior of the simpler phenylated esters, and indicate that a tautomer of the ester is the compound undergoing hydrogenation.

Experimental Part

The standard copper–chromium oxide catalyst used for the hydrogenations reported herewith was prepared as described for 37 KAF (p. **1140** of Ref. **2).** Catalysts prepared by the same method but containing calcium, strontium, magnesium or manganese **instead** of barium were also used for ethylphenylacetate. In addition catalysts *ex*-carbonate (p. **1144,** Ref. **2)** containing barium or calcium were used as well as a catalyst ex-chromate containing only copper, chromium and oxygen. The ratio of catalyst to hydrogen acceptor was usually approximately 1 g. of catalyst to 8 g. of compound. The pressure of hydrogen was usually **100–170** atm. and the reactions were carried out without a solvent in the apparatus recently described.* The nickel catalyst was usually that prepared by the ammonium carbonate method[10] and was used in the ratio of **1** g. of catalyst to **12** g. of the hydrogen acceptor. The time for the hydrogenations was usually from one to four hours.

The following exceptions to the statements made above should be noted. Three applications of catalyst were necessary in the preparation of ethyl cyclohexylacetate. Ethanol **was** used as a solvent in the preparation of o-benzylbenzoic acid, 4-phenyl-

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(8) Staudinger and Meyer, *Helv. Chim. Acta,* 5, 656 (1922); Cope and McElvain, THIS JOURNAL, 54, 4321 (1932).

(9) Adkins, Ind. *Eng. Chem., Anal. Ed.,* 4, 342 (1932).

(10) Covert, Connor and Adkins, THIS JOURNAL, 54, 1651 (1932).

butanol-1, 1,2-diphenylethane, 1,2-diphenylethanediol-1,2, and of 1,2-diphenylethanol-1. Dimethylcyclohexylamine was used as a solvent in the hydrogenation of phthalic anhydride over nickel, the reaction requiring about fourteen hours.

The ratio of products obtained in the hydrogenation of diethyl phthalate, diethyl hexahydrophthalate, ethyl benzilate varied with the length of time of reaction. The longer the time of reaction the higher the yield of hydrocarbons as contrasted with alcohols or glycols, or the yield of alcohols as contrasted with glycols.

The alcohols and glycols reported in this paper were in general characterized by their b. p. or m. p. and by the saponification value of their acetates. 4-Phenylbutanol-1 was also converted to γ-phenylbutyric acid, m. p. 48°. o-Toluic acid was characterized by its neutral equivalent. Data upon the observed physical characteristics of various products is given below: ethyl cyclohexylacetate,[11] 210–212° (740 mm.); 2 cyclohexylethanol-1,[12] 101–102° (12 mm.); o-hexahydrotoluic acid,[13] 98–99° (4 mm.); o-toluic acid,[14] m. p. 101–102°; *o*-benzyltoluene,[15] 278–285° (740 mm.); 4-phenylbutanol-1,[16] 124–127° (9 mm.); o-benzylbenzoic acid,[17] m. p. 106.5-108"; *o*-dimethylcyclohexane,[17a] 55–59° (8 mm.); o-methylhexahydrobenzyl alcohol,[18] 71–75' (3 mm.); 2,2-diphenylethanol-1,[19] 150–152° (2 mm.), m. p. 60–61°; phthalide,[20] m. p. 71–73'; o-methylbenzyl alcohol,[21] m. p 32–33°; phthalyl alcohol,[22] m. p. 65–66.5°; hexahydrophthalyl alcohol,[23] 132-133° (3 mm.), m. p. 55–56°; 1,1-diphenylethanediol-1,2,[24] m. p 118–120°; and 1,1-diphenylethane, 128–129° (8 mm.). Ethyl o-hexahydrobenzylhexahydrobenzoate (V), b. p. 155–158° (12 mm.), showed a molecular weight by saponification of 252.5, the calcd. is 252. The corresponding acid has been prepared.[25] The ester was further characterized by its conversion to o-hexahydrobenzylcyclohexylcarbinol (VI), b. p. 148–152" (10 mm.), and o-hexahydrobenzylmethylcyclohexane (VII). 125–131" (10 mm.), which were analyzed.

Anal. Calcd. for $C_{14}H_{26}O$: C, 80.00; H, 12.38. Found: C, 80.11; H, 12.27.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.60; H, 13.40. Found: C, 86.41; H, 13.25.

Summary

A number of esters containing phenyl or cyclohexyl groups have been submitted to hydrogenation over nickel and copper–chromium oxide catalysts with the production of various esters, glycols, alcohols, and hydrocarbons. The general nature of the results has been indicated in the paragraph preceding the experimental part.

A method has been described for the purification of ethyl α-phenylacetate from halogen and nitrogen containing impurities which cannot be removed by the ordinary methods of purification.

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(11) Freundler and Damond, *Compt. rend.*, 141, 593 (1905).

(12) Zelinsky, *Ber.*, 41, 2628 (1908).

(13) Skita, *Ann.*, 431, 20 (1923).

(14) Hessert, *Ber* , 11,238 (1878).

(15) Zincke, *Ann.*, 161, 94 (1872).

(16) Braun, *Ber.*, 44, 2871 (1911).

(17) Ullmann, *Ann* , 291, 24 (1896)

(17a) Eisenlohr, *Fortschr. Chem* , *Physik*, *physik. Chem.*, 18, 548 (1925).

(18) Skita, *Ann.*, 431, 20 (1923).

(19) Ramart and Amagat, *Ann. chim.*, [10] 8, 290 (1927).

(20) Wislicenus, *Ber.*, 17, 2181 (1884).

(21) Krober, *ibid.*, 23, 1028 (1890).

(22) Hessert, *ibid.*, 12, 646 (1879).

(23) Wieland, Schlichting and Langsdorff, *Z. physiol. Chem.*, 161, 74 (1926).

(24) Paal and Wiedenkaff, *Ber.*, 89, 2063 (1906).

(25) Willstätter and Waldschmidt-Leitz, *ibid.*, 54, 1423 (1921).

An extensive study of copper-chromium oxide catalysts has failed to reveal any modification of the catalyst which would bring about the production of more alcohol and less hydrocarbon in the hydrogenation of ethyl phenylacetate, than does the standard type of catalyst.

MADISON, WISCONSIN

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

The Jacobsen Reaction. III. The Monobromo Derivatives of the Three Tetramethylbenzenes[1]

BY LEE IRVIN SMITH AND CLARENCE L. MOYLE

In the previous papers of this series[2] it has been shown that when the polymethylbenzenes containing four or five methyl groups are allowed to stand in contact with concd. sulfuric acid, they first sulfonate, and then the sulfonic acids rearrange. These rearrangements are of at least two types: the first, shown by pentamethylbenzene, involves the migration of a methyl group from one molecule to another, while the second, shown by the tetramethylbenzenes, is merely a rearrangement of the methyl groups within the molecule. It was therefore of interest to investigate the monobromo derivatives of the tetramethylbenzenes, because these are pentasubstituted benzenes in which the substituents differ in nature as well as in position, and, consequently, if they were to rearrange in a manner similar to pentamethylbenzene, either a bromine atom or a methyl group could migrate and so lead to different products. There are several references in the literature to migrations of halogens among the benzene derivatives, but only two concern the bromotetramethylbenzenes. Jacobsen[3] reported that a mixture of bromodurene and concd. sulfuric acid gradually became dark and evolved considerable sulfur dioxide, and from this mixture he isolated and identified five products: *viz.*, dibromodurene, prehnitene sulfonic acid, two isomeric pseudocumene sulfonic acids, and small amounts of hexamethylbenzene. In addition to these five products, Jacobsen reported a small amount of brown amorphous material, and stated that no brominated sulfonic acids were formed. Tohl[4] investigated the action of sulfuric acid on bromoprehnitene, and reported dibromoprehnitene and prehnitene sulfonic acid as the products.

In the present work, it has been found that bromodurene, in the presence of sulfuric acid under various conditions of time, temperature and strength

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(1) Abstracted from *a* thesis by Clarence L. Moyle, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, June, 1932. Presented at the 84th meeting of the American Chemical Society, Denver, Colo., August, 1932. Paper VIII on the Polymethylbenzenes; VII, THIS JOURNAL, 64, 1614 (1932).

(2) Smith and Lux, ibid.. 51, 2994 (1929); Smith and Cass, *ibid.*, 64, 1614 (1932).

(3) Jacobsen. Ber., 20, 2837 (1887).

(4) Tohl. *ibid.*, 26, 1527 (1892).

of acid, rearranged to dibromodurene and prehnitene sulfonic acid. Based upon the equation: $2C_6H(CH_3)_4Br + H_2SO_4 \longrightarrow C_6Br_2(CH_3)_4 + C_6H(CH_3)_4SO_3H +$ I-120, the yields of dibromodurene were from 92 to 99%. The highest yield of prehnitene sulfonic acid obtained was 25%, but the reaction mixture evolved much sulfur dioxide, and 25 to 30% of the product consisted of brown or black amorphous materials. In no case was any hexamethylbenzene detected, and only traces of pseudocumene sulfonic acids were obtained. Bromoisodurene similarly gave dibromoisodurene (80% yield), prehnitene sulfonic acid (35–40% yield), and much sulfur dioxide, the dark amorphous material in this case amounting to 10–20% of the total product. No hexamethylbenzene was found, and only a trace of pseudocumene. Bromoprehnitene rearranged quickly and easily to dibromoprehnitene (99% yield) and prehnitene sulfonic acid (81% yield), the reaction requiring only about fifteen minutes, and giving rise to much less sulfur dioxide and amorphous materials than the other two bromo compounds.

These results show that, in the case of the bromotetramethylbenzenes, the bromine migrates in preference to a methyl group. Since the dibromo compound obtained is always the one corresponding to the monobromo compound used as the starting material, it is probable that the first step in the rearrangement consists of the formation of the dibromo compound and the corresponding tetramethylbenzene sulfonic acid. The latter then rearranges to the stable system prehnitene, accompanied by very small amounts of pseudocumene and hexamethylbenzene. In all these rearrangements, the first step is a sulfonation, for the bromo compounds themselves are stable in contact with phosphorus pentoxide at 80°, or when kept in a desiccator over sulfuric acid, while the sulfonic acids rearrange under these same conditions.

The gases evolved during the reactions were determined using the method already described,[2b] and the results were practically the same as those obtained in the case of the hydrocarbons. The gas is practically entirely sulfur dioxide, with only a little carbon dioxide, and the total amount of gas is about 0.38 mole per mole of bromo compound. There is no visual evidence of free bromine, and no bromide ions are present in the absorption tube. At room temperature the rate at which this gas is evolved from a 5-g. sample is very slow during the first fifteen to twenty hours (sulfonation), then fairly constant for about one hundred-sixty hours, after which it was very slow. For a 10-g. sample, the evolution of sulfur dioxide continues for about 360 hours, and then falls off. A great deal of this sulfur dioxide may come from secondary reactions, for the rearrangement of the bromo compounds to the dibromo compounds is complete at room temperature in one or two days, while the evolution of sulfur dioxide continues for two or three weeks, and it is significant that while the brown amorphous by-product does not contain sulfur, yet, when placed in contact with sulfuric acid, much sulfur dioxide is evolved.

The velocity and direction of the reaction of the bromo compounds with sulfuric acid is affected to a great degree by the temperature, for there appear to be upper and lower limits, outside of which the sulfonic acid merely hydrolyzes to the hydrocarbon, no rearrangements taking place Thus bromodurene and concd. sulfuric acid gave little or no reaction in twenty-five hours at 10–15°, while at 25° complete rearrangement occurred. Using bromodurene sulfonic acid and sulfuric acid at 10–15°, about 85% of the sulfonic acid was hydrolyzed to bromodurene in twenty-five hours, while at 25–30' the *rearrangement* was complete in the same time; at 60–80°, the *rearrangement* required about thirty minutes; while at higher temperatures (130–150°), hydrolysis again became the chief reaction. The most favorable temperatures for the rearrangement are from 25 to 30°, for although somewhat higher temperatures increase the speed of the rearrangement, they also increase the amounts of amorphous by-products formed.

Experimental Part

The Jacobsen Reaction.—One experiment will be described, and the results of others given in tabular form. Bromodurene (0.1 mole, m. p. 60.5°) was mixed with eight times its weight of concd. sulfuric acid in a loosely stoppered 250-cc. flask, and set aside at room temperature (25–30°) with occasional shaking. After one hour, the mixture became pink, after twelve hours it became brown, and then slowly changed to dark brown-black. During the first twelve hours, small amounts of sulfur dioxide were evolved, which increased in rate, reaching a maximum and fairly constant rate after the second day, and continuing so for 5 days, after which the sulfur dioxide evolved decreased very much. At the end of ten days the mixture was poured onto 300 g. of ice, the lumps broken up, and then filtered. The insoluble material was dried on a porous plate and extracted thoroughly with petroleum ether, followed by chloroform. A black, insoluble carbon-like residue remained; wt., 0.6 g. The chloroform extractions were evaporated, yielding 4.8 g. of a brown, amorphous powder. The petroleum ether extractions were decolorized with norite and set aside to crystallize, yielding 13.4 g. (91.8%) dibromodurene, white needles, m. p. crude, 184–191°. This contained a little monobromodurene which was removed by repeated crystallization, after which the dibromo compound weighed 11.2 g. and melted at 200°. The dibromo compound was identified by its melting point and mixed melting point; by reducing it with hydriodic acid and red phosphorus at 225°, it gave a 90% yield of durene, m. p. 79.5–80.0°. No traces of hexamethylbenzene were detected in the water-insoluble chloroform-soluble products.

The aqueous filtrate, containing the water-soluble products of the reaction, was decolorized by boiling for five minutes with 2 g. of norite. It was then filtered and the filtrate evaporated until the temperature rose to 110°. On cooling to 0° there resulted 3.2 g. of a sulfonic acid (m. p. 89–92") which after three crystallizations melted at 101°. It was prehnitene sulfonic acid (m. p. 103°) identified by mixed m. p., and by conversion to the sulfonamide melting at 186° (m. p., and mixed m. p.).

The filtrate from the sulfonic acid was hydrolyzed by passing steam through it at 145°. About 0.2 cc. of oil came over into the distillate. This oil gave a nitro compound melting at 182.5–183.5° which was identified as trinitropseudocumene by its mixed melting point with an authentic specimen (m. p. 184°).

TABLE I

PRODUCTS OF THE JACOBSEN REACTION UPON THE BROMOTETRAMETHYLBENZENES

Expt.	Subs.	Wt., g.	Time	Temp., °C.	Dibromo cpd., g.	Prehnitene sulfonic acid, g.	Pseudo-cumene from hydrolysis of S. A. filtrates	Total amorphous materials, g.	Remarks
1	Bromodurene	21.3	10 days	25–30	13.4	3.2	0.2 cc.	5.4	
2	Bromodurene	5.0	7.5 days	25–30	3.8	0.1	None	1.6	
3	Bromodurene	10.0	16.5 days	25–30	6.6	.9	None	2.6	
4	Bromodurene	15.0	4 hours	80	9.3	.1	None	4.0	
5	Bromodurene[a]	10.0	5 minutes	75[b]	6.1	.5	None	2.4	
6	Bromodurene[c]	10.0	100 days	25–30	6.8	None	None	2.5	
8	Bromodurene	5.0	5 hours	75	..	...	..	...	
10	Bromodurene sulfonic acid	5.0	1 day	30	1.5	0.3	..	1.2	
11	Bromodurene S. A.[d]	5.0	6 weeks	25–30	1.1	.1	..	0.8	
12	Bromoisodurene[e]	10.0	10 hours	25–30	5.5	2.1	..	1.0	
13	Bromoisodurene[e]	20.0	30 min.	60	8.3	3.6	0.1 cc.	3.7	5.6 g. recovered monobromo cpd.
15	Bromoprehnitene[e]	10.0	15 min.	25–30	3.4	2.4	..	0.1	5.0 g. recovered monobromo cpd.
16	Bromoprehnitene	10.0	15 min.	25–30	3.3	2.4	..	.2	4.8 g. recovered monobromo cpd.

[a,b] With 20 cc. of a mixture of 2 parts of concd. sulfuric acid and 1 part of 60% fuming sulfuric acid. Started at room temp.; temp. rose to 75°. [c] Bromo compound dissolved in chloroform and shaken with sulfuric acid. All the bromodurene was recovered unchanged. [d] Merely stood in a desiccator over sulfuric acid for six weeks. [e] With 4 parts (by vol.) of a mixture consisting of 35 cc. of concd. sulfuric acid and 5 cc. of 60% fuming sulfuric acid.

Blank experiments on the monobromotetramethylbenzenes showed them to be perfectly stable in contact with phosphorus pentoxide or in desiccators *over* sulfuric acid. Similar experiments showed the dibromotetramethylbenzenes to be stable when *in contact* with sulfuric acid for two months; beyond a slight darkening, and evolution of a little sulfur dioxide, there was no change and 95% of the material was recovered pure.

In identifying the dibromo compounds, it was found that the mixed melting points with authentic specimens were of little use, because the depressions are so small that direct identification by this means becomes very uncertain. However, it was found that the dibromo compounds could be converted to the corresponding hydrocarbons in 90% yields by heating them to 225° with hydriodic acid and red phosphorus for a few hours. Durene was identified directly in this way, since it is a solid, while prehnitene and isodurene were identified by converting them to the dinitro compounds and comparing these with authentic specimens. While the two dinitro compounds melt fairly close together, all the possible binary mixtures of the three dinitro compounds show melting point depressions of 15° or more, against depressions of only about 2° for the mixtures of the dibromo compounds. These results are shown in Table II.

TABLE II

MIXED MELTING POINTS OF THE DIBROMO- AND DINITROTETRAMETHYLBENZENES

Dibromo compounds	Dinitro compounds
Isodurene (199) + prehnitene (208), 198–201°	Isodurene (181) + prehnitene (176), 155–165'
Isodurene (199) + durene (200), 198–199°	Isodurene (181) + durene (206–207), 165–178°
Prehnitene (208) + durene (200), 203–204°	Prehnitene (176) + durene (206–207), 162–169°
	Isodurene (181) + trinitropseudocumene (184), 161–167°

Gaseous Products of the Reaction.—Experiments 2 and 3 were carried out in closed systems, sweeping a slow current of nitrogen through the apparatus and collecting the gaseous products in a suitable absorption train.[2] Experiment 2 was run for 180 hours, and experiment 3 for 360 hours. The weight of the gaseous products was very small during the first twenty-four hours, then it increased quite rapidly during the next 125 (experiment 2) or 250 hours (experiment 3), after which the hourly production of gas became very small again. The results are given in the table below.

TABLE III

RESULTS OF ANALYSES OF THE GASEOUS PRODUCTS

Bxpt.	Total gas evolved (Gain in *wt.* of KOH bulb)	SO_2 as sulfite	SO_2 as sulfate	CO_2	Mole ratio, bromo cpd. to *av.* SO_2
2	0.5560	0.5284	0.5381	0.0261	0.356
3	1.1505	....	1.0920	.0599	.363

The liquid in the absorption bulbs contained no sulfides, and only faint traces of halides.

Preparation of Materials

Bromodurene.[5]—Durene (50 g.) was dissolved in carbon tetrachloride (100 g.) in a 500-cc. 3-necked flask provided with separatory funnel, stirrer and exit tube. A crystal of iodine was added, the flask cooled in an ice-bath and then a solution of 62.7 g. of

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(6) Jacobsen, *Ber.*, 20, 2837 (1887).

bromine (5% excess) in 60-cc. of carbon tetrachloride was slowly added. The flask was kept out of direct sunlight during the bromination. The bromine was added during one and one-half hours, after which the mixture was stirred at room temperature for one hour longer. The product was washed with 200 cc. of 5% sodium hydroxide, then thoroughly with water. The carbon tetrachloride was removed by distillation through a short column, the residue boiled for thirty minutes with a solution of 4 g sodium in 100 cc. ethyl alcohol, and then allowed to stand overnight Water (900 cc.) was added, the precipitated solid filtered and dried; wt. 77.5 g. (calcd. 79.5). It was purified by steam distilling it for five hours to remove small amounts of dibromo compound. The monobromo compound was removed from the distillate by filtration, and then crystallized from 95% ethyl alcohol. It was pure white, weighed 62.8 g., and melted at 60.5°.

Bromoprehnitene and Bromoisodurene.—The hydrocarbon (50 g.) was dissolved in glacial acetic acid (100 cc.) containing a crystal of iodine, and brominated with a solution of 62.7 g. of bromine in 62 cc. of acetic acid, using the same apparatus and conditions given above for bromodurene. The reaction product was poured into water at 0°, whereupon a solid separated out. The water was decanted off, and the solid washed thoroughly with alkali followed by water (all washings at 0°). The solid was crystallized from alcohol at −15° and was then fractionated through a short packed column. Bromoisodurene, b. p., 140–142° (22 mm.). n_D^{28} 1.5614, m. p. 7.5–8.5°; yield 34.8 g. from 25 g. of isodurene (calcd. 39.7 g.). Bromoprehnitene, b. p. 140–141° (30 mm.), n_D^{22} 1.5650, m. p. 29–30°; yield 59.8 g. from 50 g. of prehnitene (calcd. 79.4 g.).

Dibromo Compounds.—The hydrocarbon (10 g.) was dissolved in 30 cc. of glacial acetic acid, a crystal of iodine added, and then brominated, with stirring, by adding a solution of 25 g. of bromine in 20 cc. of acetic acid. The bromine was added during ten minutes, after which the reaction mixture stood for one hour. The resulting mass of liquid and solid was diluted with water, the liquid decanted, and the residual solid washed with alkali followed by water, after which it was filtered and dried. The solid obtained in this way was white and weighed 19–21 g. (calcd. 21.8). The dibromo compounds were purified by repeated crystallization from chloroformalcohol, by dissolving them in hot chloroform, adding hot alcohol and boiling until crystallization began. The melting points are given in Table II.

Bromodurene Sulfonic Acid, $C_6Br(CH_3)_4SO_3H\cdot 1.5H_2O$.—Bromodurene (21.3 *g.)* was stirred for five minutes at 0° with 60 cc. of a mixture of *2* parts of concd: sulfuric acid and 1 part of 60% fuming sulfuric acid. The reaction mixture was poured onto 500 g. of ice and the resulting aqueous solution extracted once with chloroform. It was then cooled to 0° and 200 cc. of concd. sulfuric acid carefully added with stirring, keeping the temperature below 25°, but adding the acid as quickly as possible since the sulfonic acid is slowly hydrolyzed in contact with the mineral acid. The precipitated sulfonic acid was filtered through cloth, and was recrystallized twice from 20% hydrochloric acid. The dried acid weighed 16.7 g., m. p. 142–143° (dec.).

Anal. Calcd. for $C_6Br(CH_3)_4SO_3H$: Br, 25.0; S, 10.0. Found: Br, 24.8; S, 9.98. Water of hydration (loss in weight in vac. desiccator over $CaCl_2$ for twenty-four hours) 8.5%; calcd. for 1.5 H_2O, 8.4%.

Bromodurene Sulfonyl Chloride.—The dried sodium sulfonate was treated with 1.5 times its weight of phosphorus pentachloride for one hour. The reaction mixture was treated with water, the solid filtered off and recrystallized twice from ether as white prisms, m. p. 185°.

Bromodurene Sulfonamide.—The sulfonyl chloride was heated with concd. ammonium hydroxide for fifteen minutes, the reaction mixture cooled and the solid filtered off and crystallized from alcohol; m. p. 194°.

Summary

1. The Jacobsen reaction on the bromotetramethylbenzenes consists in the migration of a bromine atom to give the corresponding dibromo compound and prehnitene sulfonic acid. The usual by-products of sulfur dioxide and a brown amorphous material are obtained.

2. The first step in the reaction is sulfonation, and the sulfonic acid is the rearranging molecule.

3. Whether the reaction consists of the rearrangement or merely hydrolysis of the sulfonic acid, depends on the temperature. At very low and very high temperatures, the main reaction is hydrolysis. The best temperature for the rearrangement is from 25 to 65°.

4. The dibromo compounds cannot be identified by their mixed melting points, as the depressions are only about 2°, but the dinitro compounds give depressions of 15° or more and the series dibromo compound, hydrocarbon, dinitro compound can be used as a method of identification.

5. The dibromo compounds do not rearrange in contact with sulfuric acid.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Preparation of Substituted Vanillic Acids

BY L. CHAS. RAIFORD AND DWIGHT J. POTTER

Benzaldehyde[1] and anisaldehyde[2] are easily oxidized by air to the corresponding acids. *p*-Hydroxybenzaldehyde[3] and protocatechuic aldehyde[4] are more resistant and are not oxidized readily by potassium permanganate solution but require fusion with caustic potash to give the acids. Tiemann[5] found that treatment of vanillin solutions with oxidizing agents caused hardly any change, or else complete decomposition, depending on conditions. Vogel[6] prepared 5-nitrovanillic acid, and Brady and Dunn[7] obtained the 5-bromo compound by hydrolysis with alkali of the corresponding nitriles which, in turn, had been obtained from the respective oximes. Bromovanillin could not be oxidized by acetic acid solution of chromic acid or by alkaline permanganate.

The recent syntheses in this Laboratory of all chlorine and bromine

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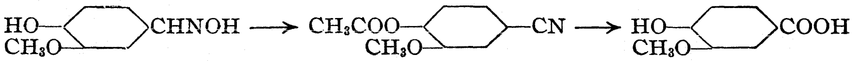
(1) Wöhler and Liebig, *Ann.*, 3, 250 (1832).
(2) Cahours, *ibid.*, 56, 308 (1845).
(3) Bücking, *Ber.*, 9, 529 (1876).
(4) Fittig and Remsen, *Ann.*, 159, 150 (1871).
(5) Tiemann, *Ber.*, 9, 415 (1876).
(6) Vogel, *Monatsh.*, 20, 389 (1899).
(7) Brady and Dunn, *J. Chem. Soc.*, 107, 1860 (1915).

substitution products of vanillin required by theory provided material from which the corresponding acids might be prepared. Since the latter cannot be obtained by oxidation of the aldehydes in the usual ways the methods of Vogel and of Brady and Dunn were tested further. The oximes, prepared as directed in the literature,[8] were converted by boiling with acetic anhydride into the acetoxynitriles, and the latter were hydrolyzed by solution of potassium hydroxide, as indicated below.



In general, good yields of acid were obtained in this hydrolysis, and the effect of steric hindrance was noted only when both ortho positions were substituted. In the case of 2,6-dibromovanillin (CHO=1) none of the required acid was isolated, but 87% of the nitrile, m. p. 215°, was recovered.[9]

Experimental Part

5-Bromo-6-chlorovanillin Oxime.—This was obtained in 79% yield by refluxing for one hour a mixture containing 12 g. of the required vanillin, 4 g. of hydroxylamine hydrochloride, 3.2 g. of anhydrous sodium carbonate dissolved in 100 cc. of alcohol and 20 cc. of water, and finally adding water to the hot liquid to precipitate the product. Recrystallization from dilute alcohol gave fine colorless needles, m. p. 203–204° with apparent decomposition.

Anal. Calcd. for $C_8H_7O_3NClBr$: X, 41.17. Found: X, 40.61.

The isomeric 5-chloro-6-bromovanillin oxime was obtained in 81% yield as described above. Crystallization from dilute alcohol gave colorless needles; m. p. 203–204° with decomposition. A mixture of the oximes melted at 200°.

Anal. Calcd. for $C_8H_7O_3NClBr$: X, 41.17. Found: X, 40.65.

Preparation of **Acetoxynitriles.**—A mixture of the oxime and slightly more than three times its weight of acetic anhydride was gently boiled for an hour under a reflux condenser, and the resulting liquid poured into several volumes of ice and water which was being stirred mechanically. In many instances the product separated as an oil, but neutralization with potassium hydroxide and stirring caused it to solidify. The composition and general properties are recorded in Table I.

Hydrolysis of **the Nitriles.**—To avoid the difficulty involved in the use of hot alkali solution on glass vessels and the consequent contamination of products with silica attempts were made to hydrolyze the nitriles with 90% sulfuric acid.[10] Experiment showed that this would cause much loss by charring and make it difficult to secure any pure product. The method adopted was to boil the nitrile with 6 *N* potassium hydroxide solution under a return condenser until no more ammonia was evolved. The cooled mixture was then acidified by concentrated hydrochloric acid, cooled again, the precipitated acid collected and crystallized from a suitable solvent. The effect of halogen substitution in the time required for hydrolysis, and the composition and properties of the acids are indicated in Table II.

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(8) Raiford and others, THIS JOURNAL, 52, 4576 (1930).

(9) The composition was checked by bromine determination. *Anal.* Calcd. for $C_8H_5O_2NBr_2$: Br, 52.11. Found: Br, 51.97.

(10) Sudborough, J. Chem. *Soc.*, 67, 602 (1895).

TABLE I

3-METHOXY-4-ACETOXYBENZONITRILE AND HALOGEN SUBSTITUTION PRODUCTS

Substituents	Yield, %	Solvent	Crystal form	Formula	M. p., °C.	Halogen analyses, % Calcd.	Found
Acetoxyvanillonitrile (unsubstituted)	94[a]	Water	Colorless needles	$C_{10}H_9O_3N$	110	...	...
2-Bromo-	Nearly quant.	Dil. alc.	Colorless needles	$C_{10}H_8O_3NBr$	71- 72	29.63	29.53
2,6-Dibromo-	98	*n*-Butanol	Nearly colorless needles	$C_{10}H_7O_3NBr_2$	143-144[b]	45.85	45.66
2,5,6-Tribromo-	97	Alc.	Nearly colorless needles[c]	$C_{10}H_6O_3NBr_3$	174-175	56.05	55.86
5-Chloro-	Nearly quant.	Isobutanol	Thick yellow needles	$C_{10}H_8O_3NCl$	133-134	15.73	15.61
6-Chloro-	95	HAc	Fine colorless needles	$C_{10}H_8O_3NCl$	131-132	15.73	15.78
5,6-Dichloro-	Nearly quant.	Dil. HAc	Colorless scales	$C_{10}H_7O_3NCl_2$	143-144	27.28	26.75
5-Bromo-6-chloro-	Nearly quant.	Dil. HAc	Pale yellow needles	$C_{10}H_7O_3NClBr$	165	37.94	37.91
5-Chloro-6-bromo-	90	Alc.	Colorless powder	$C_{10}H_7O_3NClBr$	176	37.94	37.47

[a] This product was isolated by Marcus [*Ber.*, **24**, 3654 (1891)] but no yield was recorded. [b] A mixture of this and the corresponding oxime, m. p. 144–145°, melted at 115–120°. [c] Exposure to light caused the crystals to develop a grayish-yellow color.

TABLE II

ACIDS OBTAINED BY HYDROLYSIS OF SUBSTITUTED ACETOXYVANILLONITRILES

Substituents	Time, hours	Yield, %	Solvent	Crystal form	Formula	M. p., °C	Halogen analyses, % Calcd.	Found
Unsubstituted	1	93[a]	Alc.	Colorless needles	$C_8H_8O_4$	207-208	...	...
2-Bromo-	4	Nearly quant.	Water	Colorless needles	$C_8H_7O_4Br$	163-164	32.39	32.72
5-Bromo-	2	98[b]	Alc.	Colorless needles	$C_8H_7O_4Br$	231-232[b]	32.39	32.41
5,6-Dibromo-	48	78	Water	Nearly colorless needles	$C_8H_6O_4Br_2$	199-200[c]	49.08	48.80
2,5,6-Tribromo-	54	70	Dil. alc.	Nearly colorless flakes	$C_8H_5O_4Br_3$	231-232 Decomp.	59.25	59.63
5-Chloro-	2	95	Dil. HAc	Fine colorless needles	$C_8H_7O_4Cl$	244-245	17.55	17.45
6-Chloro-	3	78	Dil. HAc	Colorless leaflets	$C_8H_7O_4Cl$	207	17.55	17.66
5,6-Dichloro-	10	Nearly quant.	Water	Straw colored needles	$C_8H_6O_4Cl_2$	184-185[d]	29.92	29.85
5-Bromo-6-chloro-	13	80	Water	Nearly colorless needles	$C_8H_6O_4ClBr$	196-197[e]	41.01	40.84
5-Chloro-6-bromo-	13	85	Very dil. alc.	Straw colored needles	$C_8H_6O_4ClBr$	187-188[f]	41.01	41.12

[a] On record, but not obtained by this method or in this yield. [b] Found, also, for a sample prepared by bromination of vanillic acid. Both samples darken and shrink about 223° and evolve gas slowly at the melting point. Brady and Dunn recorded 221°. They found 179° for 5-bromovanillin oxime, but noted no decomposition in either case. In the present work slow heating caused the oxime to decompose with evolution of gas about 170°; with rapid heating it melts to a clear liquid at 179° and decomposes a few seconds later. [c] Dried to constant weight at 120–130°: 0.3665 g. lost 0.0106 g. Calcd. for $C_8H_6O_4Br_2 \cdot 0.5\,H_2O$: H_2O, 2.69. Found: H_2O, 2.89. [d] Attempts to determine water of hydration directly were unsatisfactory because of slow sublimation on heating. *Anal.* Calcd. for $C_8H_6O_4Cl_2 \cdot 0.5H_2O$: Cl, 28.83. Found: Cl, 28.95. [e] Calcd. for $C_8H_6O_4ClBr \cdot 0.5H_2O$: Hal., 39.74. Found: Hal., 40.01. [f] Calcd. for $C_8H_6O_4ClBr \cdot 0.5H_2O$: Hal., 39.74. Found: Hal., 39.69.

Summary

1. Chlorine and bromine as substituents in vanillin oxime cause no appreciable hindrance in the formation of the acetoxynitriles.

2. The acetoxynitriles may be hydrolyzed by caustic potash solution to give high yields of the corresponding acids, unless both ortho positions are substituted. When the 2,6-dibromo compound was used no acid was obtained but 87% of the nitrile was recovered. So far as examined,. the chlorine derivatives are more reactive than the bromine compounds.

3. Each of the four 5,6-dihalogenated vanillic acids studied crystallized from water with half a molecular proportion of solvent of crystallization

4. Further work is in progress.

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The Resolution of β-Ethoxyamines

BY WALLACE R. BRODE AND I. J. WERNERT

In an earlier paper[1] a method has been described for the synthesis of β-ethoxyamines. The present paper describes the complete resolution of β-ethoxyhexylamine and β-ethoxy-β-phenylethylamine and the partial resolution of β-ethoxybutylamine and β-ethoxyamylamine. The resolution of these amines proved to be extremely difficult. There appeared to be no marked difference in the solubility of the acid tartrate or camphor sulfonate salts of the d- and *l*-amines, and in addition there was a tendency to form gels which could not be filtered. In certain of the cases studied, more than twenty fractional crystallizations failed to yield a salt of constant rotation. In other cases a salt of constant rotation was obtained in two or three recrystallizations, and although fifteen to twenty additional crystallizations failed to change its rotation, the activity of the amine recovered from the mother liquor and the complete resolution of the amine by other resolving agents showed that only a partial resolution had been effected.

Considerable doubt may exist as to the completeness of a resolution if a statement indicating the constancy of the rotation of the salt or even the specific rotation of the salt is omitted. If the maximum rotation of the final pure salt were included, the repetition of the resolution by others would be greatly facilitated. A second consideration that is often overlooked in the resolution of asymmetric compounds is a determination of the rotation of the active compound that may be obtained by the hydrolysis of mother liquors which contain the more soluble fraction. In the case of the attempted resolution of β-ethoxy-β-phenylethylamine

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[1] Wernert and Brode, THIS JOURNAL, 54, 4365 (1932).

as described in this paper, the resolution was apparently complete, in that the less soluble fraction had reached a constant rotation which was not altered by more than ten additional crystallizations, yet the more soluble fraction from the mother liquors gave an amine with a rotation of +16.2°, while the amine obtained from the supposedly pure crystals of constant rotation had an activity of only −4.3°. An incomplete examination of the literature shows that, while in most cases no mention is made of the rotation of the active compound obtained from the mother liquors, there are a few cases[2,3,4] reported in which the rotation of the asymmetric compound from the mother liquor was actually reported as higher than that of the supposedly pure material obtained from the less soluble fraction. The existence of these known cases, together with the absence of data on the activity of the mother liquor or more soluble compound, would tend to leave some uncertainty with regard to the completeness of some resolutions.

Experimental and Discussion

Partial Resolution of β-**Ethoxybutylamine.**—This resolution was first attempted with d-tartaric acid: 35.8 g. of amine was dissolved in 275 cc. of absolute alcohol and added to 47.2 g. (5% excess) of d-tartaric acid dissolved in 300 cc. of absolute alcohol. On cooling to 0°, the mass congealed and it was necessary to centrifuge in order to separate the solid matter from the alcohol solution. The separation of the two forms by fractional crystallization was so slow that there was no evident approach to a constant rotation. After more than 20 fractionations 4 g. of product having a specific rotation of +34.5° was obtained. On the opposite end of the series 17 g. of crystals was obtained from the mother liquors of the most soluble fractions which gave a specific rotation of +10.1°. Evidently a separation of the optical antipodes was taking place but the failure to obtain a constant rotation in the less soluble fraction indicated that only a partial resolution had been effected. The resolution was then undertaken with d-camphorsulfonic acid as the resolving agent; 109.3 g. of d-camphorsulfonic acid was added to 52.6 g. of β-ethoxybutylamine dissolved in 200 cc. of ethyl acetate. The first crystals which separated out on cooling had a specific rotation of +16.4°. After eight recrystallizations the less soluble fraction had a rotation of $19.7". Three additional fractionations gave salts with rotations of $20.5, $19.3 and +19.6°, respectively. The material having a specific rotation of +19.6° amounted to 48.5 g. The free amine was prepared from this fraction by treatment with an excess of a concentrated sodium hydroxide solution and extraction with ether. The ethereal extract was dried over solid sodium hydroxide and on distillation yielded 10.5 g. of amine, b. p. 137.5–138.5"; 0.5738 g. of the amine in 25 cc. of absolute alcohol gave $[\alpha]^{25}_{\mathrm{D}}$ +7.9°. The gum-like mass which resulted upon concentration of the most soluble fractions was decomposed with sodium hydroxide in the same manner as the less soluble salt. Eleven grams of the amine was obtained, b. p. 62.5–63.5° at 48 mm.; 0.4850 g. of the amine in 25 cc. of absolute alcohol gave $[\alpha]^{25}_{\mathrm{D}}$ −11.3'. The greater activity of the more soluble fraction would indicate that only a partial resolution had been effected.

Partial Resolution of β-**Ethoxyamylamine.**—*d*-Camphorsulfonic acid did not form a well-defined crystalline salt with this amine so that d-tartaric acid was the only resolv-

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(2) Fischer and Scheibler, *Ann.*, 383, 344 (1911).

(3) Pierre and Billon, Ann. *chim.*, 7, *350* (1927).

(4) Fujisi, *Sci.* Papers *Inst. Phys.-Chem. Research (Tokyo), 8,* 161 (1928).

ing agent used in an attempt to separate the isomeric forms of this base; 250 g. of β-ethoxyamylamine in 500 cc. of 95% ethyl alcohol was added to 286 g. of d-tartaric acid dissolved in a solution of 500 cc. of 95% alcohol and 50 cc. of water. On cooling the amine acid tartrate separated out in a solid unfilterable mass. Dilution with alcohol to a total volume of 3.5 liters still gave a solidified gel-like form which had to be centrifuged to separate the solid from the solvent. Recrystallization and centrifuging again gave 149 g. of a salt, $[\alpha]^{25}_{D}$ +15.7°. Eight recrystallizations produced a salt with a rotation of +28.6°, each fraction having a product of higher rotation than that of the preceding fraction. Examination of the end fractions of the more soluble salt showed salts of +11.6 and +9.6° for the last two fractions. In view of the fact that at no time during the fractionation were well-defined crystals formed and that the amount of the end fractions were rather small, with no indication of a constant rotation, it was not possible to carry the fractionation to completion.

Resolution of β-Ethoxyhexylamine.—This amine did not form a well-defined crystalline salt with d-camphorsulfonic acid, so the resolution was attempted only with *d*-tartaric acid. The d-acid tartrate was formed by the reaction of 335 g. of β-ethoxyhexylamine in 500 cc. of 95% alcohol with 346 g. of d-tartaric acid dissolved in 500 cc. of 75% alcohol. The solution was made up to a volume of 1.5 liters by the addition of 50% alcohol and on cooling deposited 280 g. of salt which was separated by centrifuging, $[\alpha]^{25}_{D}$ +8.4°. Subsequent recrystallization from 95% alcohol gave rotations of +1.01, –2.8, –4.5 and –5.8" for the second, fourth, sixth and eleventh recrystallizations. The less soluble middle fractions were then worked up until they gave a rotation of –5.9° and combined with this latter fraction. A yield of 102 g. of this salt was obtained; it formed short thick needles, m. p. 119.5–120.5". The free amine was obtained by treatment with sodium hydroxide in the manner previously described. Sixteen grams of amine was obtained from 35 g. of salt, b. p. 70.5–70.7° (at 14 mm.); 0.5288 g. made up to 25 cc. in 95% alcohol gave $[\alpha]^{25}_{D}$ –24.6'. After the removal of several intermediate fractions from the mother liquor, the liquid residue was cooled to 0°. An amorphous residue was obtained which was centrifuged, washed with alcohol and finally recrystallized from 95% alcohol; 100 g. of this material was obtained, $[\alpha]^{25}_{D}$ +14.6°. After six recrystallizations a rotation of $[\alpha]^{25}_{D}$ \$24.2" was obtained, which was not increased by two additional recrystallizations. Forty grams of this salt was decomposed with saturated sodium hydroxide solution as previously described. A yield of 16 g. of amine, b. p. 70.8–71.2° (at 15 mm.) was obtained. 0.6242 g. in 25 cc. of 95% ethyl alcohol gave $[\alpha]^{25}_{D}$ +8.6°.

Resolution of β-Ethoxy-β-phenylethylamine.—One hundred grams of β-ethoxy-β-phenylethylamine was dissolved in 300 cc. of ether and 147 g. (5% excess) *d*-camphorsulfonic acid was added to the solution in small portions, together with 450 cc. of ethyl acetate. The solution was heated during this process and upon cooling 130 g. of short well-defined crystals separated; 0.2270 g. of these crystals in 10 cc. of water gave $[\alpha]^{25}_{D}$ +13.2°. Recrystallization of this salt six times from ethyl acetate produced little change in the rotation. A final yield of 63 g. of salt was obtained which had a rotation of $[\alpha]^{25}_{D}$ +11.4° (m. p. 139–40°). Treatment of this salt with an excess of concentrated sodium hydroxide solution and extraction yielded the amine, b. p. 102–103° (at 10 mm.); 0.7003 g. in 25 cc. of ethyl alcohol gave $[\alpha]^{25}_{D}$ –4.3°. After separation of several intermediate fractions, the mother liquors were evaporated to dryness and the gum-like residue which could not be crystallized was hydrolyzed with sodium hydroxide and extracted with ether. An amine, b. p. 102–103° at 10 mm., was obtained, 0.7493 g. of which in 25 cc. of 95% ethyl alcohol gave $[\alpha]^{25}_{D}$ +11.8°.

Since over half of the camphorsulfonate salt had a nearly constant rotation, and the rotation of the recovered amine from the more soluble fraction was considerably higher than the amine from the less soluble fraction, the entire resolution was again repeated.

In the second resolution results were obtained which were identical with those of the first resolution. This d-camphorsulfonate salt ($[\alpha]^{25}_{D}$ +11.0°) was recrystallized from a number of organic solvents such as acetone, xylene, cyclohexane, diethyl ether, etc. Within the limits of observational error there was no change in the rotation of these recrystallized salts. The failure to effect a resolution, although a salt of constant rotation was obtained, would argue for the existence of some form of racemic compound which resists fractional crystallization. Such an effect has been noted in the resolution of other organic compounds.[5,6,7]

With the failure of the d-camphorsulfonate method of resolution the d-acid tartrate was tried. The crystals obtained from the d-acid tartrate salts were not as well defined as those from the d-camphorsulfonate salts, and the earlier fractionations gave distinct gels which could only be separated by centrifuging. Upon the gradual separation of the salts into the enantiomorphic forms the crystalline character improved and the final fractions were recrystallized with ease. Ninety grams of β-ethoxy-β-phenylethylamine was dissolved in 1200 cc. of alcohol to which was added 81.7 g. of d-tartaric acid. Fractional crystallization through seven series of fractionations caused only a slight rise in the rotation of the less soluble salt. On the eighth and ninth fractionations there was a distinct rise in the rotation of the less soluble fraction, together with a distinct decrease in the rotation of the central fractions, although the more soluble fraction had a rotation between these two. Further fractionation showed that compounds of different crystalline form were separated in the various intermediate fractions, those of a needle type being strongly dextrorotary while those of a plate type were levorotary. A careful separation of the fractions in accordance with the crystalline character of the salts showed an alternation between the two types. These were eventually concentrated into three series of needle fractions and three series of plate fractions. After some seven or eight fractionations a constant rotation of $[\alpha]^{25}_{D}$ +70.5° was reached in the less soluble (needle series), and a rotation of $[\alpha]^{25}_{D}$ −44.3–45.2° in the plate series.

Ingersoll[5] and Read, Campbell and Barker[8] have noted a similar anomaly in the resolution of dl-diphenylhydroxyethylamine, in that the first fraction of the d-camphorsulfonate gave on hydrolysis the pure d-base, while the second fraction on subsequent crystallization gave the l-base. It would appear that the solubility and rate of crystallization of the two acid tartrates were approximately the same, as would be evidenced by the slight resolution effected in the first seven fractionations. The fact that they were of markedly different crystalline character, however, might permit the possibility of one form separating from a supersaturated solution without the other form coming out of solution. Once having obtained a relatively pure form it would be a simple matter to complete the purification by fractional crystallization. In order to prove this a saturated solution was made from a mixture of equal parts of the two active salts ($[\alpha]^{25}_{D}$ +71° and −45°). It was found possible to induce the crystallization of either form by the addition of the appropriate seeding crystal. This would substantiate the suggestion of Stewart[9] that resolution is more a function of rate of crystal formation than of solubility. Ingersoll[5] and Read and Reid[10] have noted a similar effect in the inoculation of a racemic solution with a crystal of either of the isomeric forms (*d*A*d*B or *d*A*l*B) to induce the crystallization of that form from solution.

Thirteen grams of the d-salt ($[\alpha]^{25}_{D}$ +70.8°, m. p. 170.0–170.5") was dissolved in water and treated with a saturated solution of sodium hydroxide. The liberated amine was extracted with ether and distilled; 0.5609 g. of the amine in 25 cc. of ethyl alcohol

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(5) Ingersoll THIS JOURNAL, **47**, 1168 (1925); **50**, 2264 (1928); **54**, 274 (1932)

(6) Reed and Steel, J. *Chem Soc*. 910 (1927).

(7) Colles and Gibson, *ibid.*, 100 (1928).

(8) Read, Campbell and Barker, *ibid.*, 2310 (1929).

(9) Stewart and Allen, THIS JOURNAL, **54**, 4027 (1932)

(10) Read and Reid, J. *Soc. Chem.* Ind., 47, 9 (1928).

gave $\alpha = +4.70$ or $[\alpha]^{25}_{D}$ +104.5°. Ten grams of the l-salt ($[\alpha]^{25}_{D}$ −45.0°, m. p. 168.5–169°) was converted into the free amine in a similar manner; 0.5031 g. of this amine in 25 cc. of ethyl alcohol gave $\alpha = -4.19$ or $[\alpha]^{25}_{D}$ −104.2°.

Summary

A number of β-ethoxyamines have been partially or completely resolved. A study has been made of the procedure of resolution of these amines with d-camphorsulfonic acid and d-tartaric acid. It has been shown that it is possible to recrystallize a less soluble salt until a constant rotation is obtained and still not have effected a complete resolution. It is also possible that a salt may be recrystallized twenty or more times without reaching a constant rotation. If the salts of the enantiomorphic forms have a markedly different crystalline form, it is possible to crystallize either from a saturated solution of the active salt of the racemic compound (such as *d*A–*dl*B) by seeding with the pure active salt of the active compound (such as *d*A*d*B or *d*A*l*B).

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The Action of Chlorine on p-Toluenearsonic Acid under the Influence of Ultraviolet Light and its Chlorination with Hypochlorous Acid

BY CLIFF S. HAMILTON AND WILLIAM N. KING

It has been shown that the presence of phosphorus trichloride, phosphorus pentachloride[1] or ultraviolet light[2] greatly increases the rate of substitution of chlorine into the side chain of an aromatic hydrocarbon, when treated with chlorine. Book and Eggert[3] found that at a temperature of −80° it was possible to obtain a sixty to seventy per cent. yield of benzyl chloride if the reacting mixture was irradiated with ultraviolet light. *p*-Nitrotoluene has been chlorinated in the side chain, by passing the chlorine into the substance heated to 185–190°.[4]

Since toluene and especially *p*-nitrotoluene can be chlorinated in the side chain, it was thought that the analogous *p*-toluenearsonic acid, converted into the corresponding dichloroarsine by means of phosphorus trichloride and dissolved in a suitable solvent such as carbon tetrachloride, could likewise be chlorinated, the idea being to introduce one, two or three chlorine atoms into the side chain, and then by hydrolysis to obtain the corresponding alcohol, aldehyde and acid. In none of the experiments

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(1) F. Beilstein, Ann., 116, 336 (1860).

(2) Sabatier and Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co.. New York, 1922. p. 105.

(3) Book and Eggert, *Z. Elektrochem.*, 29, 521 (1923).

(4) Wachendorff, Ann.. 185, 271 (1877).

carried out in this manner was there any indication of side chain substitution. When hexachloroethane, a much higher boiling substance, was used as a solvent the 4-methylphenyltetrachloroarsine formed by the action of chlorine on 4-methylphenyldichloroarsine was decomposed and the product obtained after hydrolysis proved to be p-chlorobenzoic acid.

One of the characteristic reactions of tetrachloroarsines is decomposition according to the equation[5]

$$R\text{—}AsX_4 = RX + AsX_3$$

However, the literature indicates that most of these reactions are sealed tube reactions, at temperatures around 200°, and no record could be found of the use of chlorine in breaking the arsenic to carbon linkage under normal pressure at temperatures around 180°. Similar results were obtained at temperatures ranging between 75–120° when the reaction was carried out under the influence of ultraviolet light. At temperatures around 100°, the orange colored 4-methylphenyltetrachloroarsine would suddenly decompose into p-chlorotoluene and arsenic trichloride after being exposed to the ultraviolet light for about two hours. With continued chlorination at the same temperature and in the presence of ultraviolet light, there was a rapid gain in weight, indicating that the p-chlorotoluene was being chlorinated.

Toluene has also been chlorinated by means of hypochlorous acid,[6] the chlorine substituting in the ring or side chain, depending upon the conditions. Hypochlorous acid will chlorinate the side chain if it is more concentrated than one normal or if the temperature is above 40°. Low concentration of hypochlorous acid or low temperature will favor ring substitution.[7] The literature does not reveal an instance where toluenearsonic acids have been chlorinated by means of hypochlorous acid in an aqueous medium. It was found in the case of *p*-toluenearsonic acid that chlorine substituted in the nucleus and not in the side chain. In order to prove the position of the chlorine in the ring, the arsonic acid was converted into the corresponding tetrachloroarsine, the arsenic to carbon linkage broken by the action of chlorine under the influence of ultraviolet light, and the dichlorotoluene thus formed was chlorinated and hydrolyzed to yield 2,4-dichlorobenzoic acid. 3-Chloro-4-methylphenylarsonic acid has not been described previously.

In view of the fact that work in this Laboratory has shown that the arsenic to carbon linkage can be ruptured readily by the use of chlorine in the presence of ultraviolet light, the method should prove of value in the determination of the structure of more complex arsenicals.

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(5) La Coste and Michaelis, Ann., 201, 198 (1880).

(6) Levinstein and Bader, British Patent 134,909 (1918).

(7) Clark, Chem. News, 143, 265 (1931).

Experimental

4-Methylphenyldichloroarsine.—It was necessary to reduce p-toluenearsonic acid since it is insoluble in carbon tetrachloride. The reduction was accomplished by the action of phosphorus trichloride on the arsonic acid.[8]

4-Methylphenyltetrachloroarsine.—This was prepared by the action of dry chlorine on a carbon tetrachloride solution of 4-methylphenyldichloroarsine according to the method of La Coste and Michaelis.[9]

Chlorination with Hexachloroethane as the Solvent.—To 4-methylphenyltetrachloroarsine prepared from 10 g. of p-toluenearsonic acid was added 125 g. of hexachloroethane and the temperature held at 140° for the chlorination. The increase in weight was slow, approximately twelve hours being required for the chlorination. One hundred cc. of water was added to the reaction mixture, and after refluxing for a few minutes enough 6 *N* sodium hydroxide was added to make the mixture alkaline to litmus paper. On cooling, the hexachloroethane layer solidified and the water layer was poured off. The water layer was acidified to litmus paper with concentrated hydrochloric acid, and the white crystalline precipitate which formed was filtered off and recrystallized twice from an alcohol–water mixture; yield of p-chlorobenzoic acid 70–80%, sublimed at 230–232°. The p-chlorobenzoic acid was identified by preparing the amide, which melted at 174°. The neutralization equivalent for the obtained acid was 157.9 (calcd. 156.6).

Optional **Method.**—Ten grams of p-toluenearsonic acid, dissolved in 125 g. of hexachloroethane at a temperature of 140°, was heated to 185–190° and chlorinated for ten hours or until the weight had increased the calculated amount. The mixture was then treated as outlined above and an 80% yield of p-chlorobenzoic acid, subliming at 231°, was obtained.

Chlorination in the Presence of Ultraviolet Light.—4-Methylphenyltetrachloroarsine was prepared from 10 g. of p-toluenearsonic acid, as outlined above, and the carbon tetrachloride removed under diminished pressure. The resulting product was transferred as a liquid to a 100-cc. quartz flask fitted with a small stirrer which could be rotated rapidly, and a long condenser as well as an inlet tube for dry chlorine. The source of ultraviolet light was a carbon arc lamp placed about six inches from the quartz flask. With rapid stirring the chlorine was allowed to bubble slowly through the 4-methylphenyltetrachloroarsine at a temperature of 90–100°. After the mixture had been exposed to the ultraviolet light for two to three hours, it suddenly lost its orange color and became practically colorless. With continued chlorination in the presence of ultraviolet light, the weight of the flask increased 7.8 g. The solution was cooled to room temperature, 20 cc. of water added slowly through the condenser and then enough 6 *N* sodium hydroxide was added to make the solution alkaline to litmus paper. After refluxing the mixture with stirring for thirty minutes, it was cooled to room temperature, made acid to litmus paper with concentrated hydrochloric acid, decolorized with activated charcoal and finally made acid to Congo red paper. The p-chlorobenzoic acid which separated was filtered off and recrystallized twice from an alcohol–water mixture; yield 70–75% of the calculated amount, sublimed 230–232°; identified by preparing its amide.

In another experiment carried out as above, the chlorination was stopped at the point where the orange color of the 4-methylphenyltetrachloroarsine disappeared. The solution was subjected to fractional distillation, three fractions being collected. The first fraction (75–100°) consisted of phosphorus trichloride; the second fraction (100–130°) consisted largely of arsenic trichloride, while the third fraction (130–165°) was almost entirely p-chlorotoluene. This final fraction (130–165°) was refractionated

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(8) La Coste, Ann., 208, 16 (1881).

(9) La Coste and Michaelis, ibid., 201, 249 (1880).

and 5 cc. of a liquid boiling at 161° was obtained. It was identified as *p*-chlorotoluene by placing it in a quartz flask and chlorinating in the presence of ultraviolet light. Hydrolysis of the product as carried out above gave p-chlorobenzoic acid, which was finally converted to the amide. The fraction boiling between 100–130° was dissolved in 6 N sodium hydroxide solution, the solution made just acid with hydrochloric acid and hydrogen sulfide passed through. Arsenous sulfide precipitated out, thus identifying the fraction as arsenic trichloride.

Chlorination of p-Toluenearsonic Acid with Hypochlorous Acid

3-Chloro-4-methylphenylarsonic Acid.—Fifty grams of sodium hydroxide dissolved in 125 cc. of water was placed in a one-liter round-bottomed flask, fitted with a mechanical stirrer, chlorine inlet, and a tube to lead away the excess chlorine. The flask was placed in an ice-bath and when the temperature of the solution had fallen to 5° or less, chlorine was passed through until the solution acquired a yellow tinge. The temperature of the solution was raised to 20°, and then, with continuous stirring, 10 g. of p-toluenearsonic acid dissolved in the minimum quantity of 6 *N* sodium hydroxide was added. The hypochlorous acid was released by the action of 2 *N* hydrochloric acid on the sodium hypochlorite solution, the hydrochloric acid being added just rapidly enough to keep a plentiful supply of hypochlorous acid (bleaches Congo red paper) in the solution at all times. About eight hours were required to add sufficient hydrochloric acid to make the solution definitely acid to Congo red paper. The final addition of hydrochloric acid precipitated the arsonic acid, which was filtered off and recrystallized from a 50% alcohol–water mixture; yield 60%, m. p. > 250'.

Anal. Calcd. for $C_7H_{11}O_3ClAs$: As, 30.20. Found: 30.22, 30.39.

Structure Proof.—In order to prove that the chlorine was substituted in the meta position with respect to the arsono group, the acid was reduced to the dichloroarsine, and treated with chlorine in the presence of ultraviolet light at a temperature around 100°. The characteristic change of color was noted at the end of two hours, and then chlorination was continued in order fully to chlorinate the side chain. Following the method already outlined, 2,4-dichlorobenzoic acid was obtained, m. p. 160"

3-Chloro-4-carboxyphenylarsonic Acid.—This was prepared by the oxidation of 3-chloro-4-methylphenylarsonic acid with an alkaline solution of potassium permanganate. 3-Chloro-4-carboxyphenylarsonic acid is readily soluble in hot water, ether, and alcohol, m. p. 233°.

Anal. Calcd. for $C_6H_6O_5ClAs$: As, 26.72. Found: 26.62, 26.67.

Summary

1. When *p*-toluenearsonic acid dissolved in hexachloroethane was treated with chlorine at 180–190°, the arsenic to carbon linkage was broken, and then the methyl group of the *p*-chlorotoluene thus formed was chlorinated.

2. At 100°, in the absence of a solvent, but in the presence of ultraviolet light, 4-methylphenyltetrachloroarsine and 3-chloro-4-methylphenyltetrachloroarsine decomposed when treated with chlorine, the arsenic to carbon linkage being ruptured.

3. Chlorine was substituted in the ring by the action of hypochlorous acid on p-toluenearsonic acid. 3-Chloro-4-methylphenylarsonic acid and 3-chloro-4-carboxyphenylarsonic acid have been described for the first time.

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The Oxidation of Grignard Reagents

BY M. T. GOEBEL AND C. S. MARVEL

The oxidation of Grignard reagents by air and by oxygen was reported as early as 1903 and is a well-recognized reaction. However, the fact that the oxidation is extremely rapid and that it causes serious losses in connection with the use of the Grignard reagent are points which do not yet seem to be fully recognized. The experiments which are reported here are presented to call attention to these two considerations.

Attention was first directed to this problem by Bodroux,[1] who observed that arylmagnesium halides were readily oxidized by oxygen or air and that poor yields of the corresponding phenols were obtained by decomposing the oxidation products with acids. Shortly afterward Bouveault[2] found cyclohexanol as a by-product in the preparation of hexahydrobenzoic acid from the action of carbon dioxide on cyclohexylmagnesium chloride. In his experiments the by-product was formed to the extent of 20%. He thought that the alcohol was probably produced by oxidation of the Grignard reagent, and confirmed this view by oxidizing another Grignard reagent, benzylmagnesium chloride. This gave a yield of 80% of the theoretical amount of benzyl alcohol. Barbier and Grignard[3] obtained borneol by the oxidation of the Grignard reagent from pinene hydrochloride. Since these earlier papers, most of the oxidation studies[4] have dealt with aryl compounds which yield very complex mixtures of products.

Wuyts[4,5] studied both aromatic and aliphatic Grignard reagents and demonstrated with some degree of certainty that peroxides are intermediate products in the oxidation reaction. Under his experimental conditions ethylmagnesium bromide and cyclohexylmagnesium bromide were oxidized to give 88 and 81%, respectively, of the theoretical amounts of alcohol. Meisenheimer and Schlichenmaier[8] have studied the oxidation of methyl-, ethyl- and phenylmagnesium iodides and have reported the formation of the iodides along with the hydroxyl compounds when the oxidations were carried out in dilute solutions. In concentrated solutions the iodides were not obtained. Gilman and his students[7] have shown that several different Grignard reagents are slowly oxidized in boiling ether solutions and have pointed out that this reaction causes loss of yields

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(1) Bodroux, *Compt. rend.*, 136, 158 (1903).

(2) Bouveault, *Bull. soc. chim.*, [3] 29, 1051 (1903).

(3) Barbier and Grignard, *Bull. soc. chim.*, [3] 31, 840 (1904). See also Hesse, *Ber.*, 39, 1127 (1906); Houben, *ibid.*, 39, 1700 (1906).

(4) Wuyts, *Compt. rend.*, 148, 930 (1909); Porter and Steele, THIS JOURNAL, 42, 2650 (1920); Ivanov, *Bull. soc. chim.*, [4] 39, 47 (1926); Gilman and Wood, THIS JOURNAL, 48, 806 (1926).

(6) Wuyts, *Bull. soc. chim. Belg.*, 36, 222 (1927).

(6) Meisenheimer and Schlichenmaier, *Ber.*, 61, 2029 (1928).

(7) Gilman and Wood, THIS JOURNAL, 48, 806 (1926); Gilman and St. John, *Bull. soc. chim.*, [4] 45, 1091 (1929); Gilman and Hewlett, *Rec. trav. chim.*, 48, 1124 (1929).

in synthetic work. Gilman and Zoellner[8] have also noted that oxidation may cause losses in the carbonation of Grignard reagents.

None of these experiments indicated clearly the extreme ease with which Grignard reagents were oxidized at low temperatures. Our attention was directed to this fact by the results of attempts to combine cetylmagnesium bromide with 2,3-dibromopropene-1. The reaction was carried out in the usual manner[9] by preparing the Grignard reagent in ether, cooling this solution and adding the 2,3-dibromopropene-1. Among the products of the reaction, a large amount of cetyl alcohol was always obtained. After a number of trials it was found that this was caused by oxidation of the Grignard reagent by air. In the usual Grignard reaction the ether vapors prevent the easy access of air to the organomagnesium halide and thus oxidation is almost completely prevented. In all cases where the Grignard reaction mixture is cooled to a low temperature before the addition of another reagent, the ether vapors are largely condensed and if the reaction mixture is stirred in air a large loss of Grignard reagent due to oxidation will follow. Under ordinary circumstances this side reaction will not be recorded by the experimenter because the reagents most commonly used are the lower ones and the alcohols produced by the oxidation are lost in the low boiling fractions during purification. These statements are borne out by the experiments recorded in this paper on the absorption of oxygen by various Grignard reagents in diethyl ether.

In diethyl ether at room temperature the oxidation of 0.006 mole of Grignard reagent was 80–90% complete in one hour. At 0° with slow stirring the Grignard reagent was completely' oxidized in six to eight minutes and with rapid stirring four to five minutes was sufficient time for the reaction to go to completion It is of interest to note that phenylmagnesium bromide is more slowly and less completely oxidized than is the case for any of the alkyl magnesium halides which have been studied. These figures must of course be considered as qualitative rather than strictly quantitative as no elaborate precautions were taken in carrying out the experiments.

The completeness of the oxidation and the fact that an alcoholate was produced was demonstrated by oxidizing 0.242 mole of n-octylmagnesium bromide in diethyl ether and the isolation of 0.21 mole of n-octyl alcohol. Similarly cetylmagnesium bromide gave about 60% of the theoretical amount of cetyl alcohol.

Experimental

Preparation of Grignard Reagents.—The ether solutions of these reagents were prepared and standardized by titration by the methods recommended by Gilman and his students.[10]

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(8) Gilman and Zoellner, THIS JOURNAL, **53, 1945 (1931)**.

(9) Lespieau and Borguel, "Organic Syntheses," **Vol.** VI, 1926, p. 20.

(10) Gilman and others, THIS JOURNAL, 46, **150, 159. 2462 (1923); 61, 1576 (1929)**.

Experiments on Oxidation at Room Temperature.—An Erlenmeyer flask, mounted on a shaking machine, was connected with a gas measuring buret. The apparatus was filled with oxygen and 35 cc. of dry ether was introduced into the flask through a dropping funnel. The pressure was adjusted by a leveling bulb. Then a measured quantity of a standard solution of the Grignard reagent was added through the dropping funnel. The flask was vigorously agitated by the shaker and the absorption of oxygen was noted by the change in pressure. A thermometer in the ether gave the temperature.

TABLE I

OXIDATION OF GRIGNARD REAGENTS IN DIETHYL ETHER AT ROOM TEMPERATURE

No.	Grignard reagent	Temp., °C.	Reagent used, mole	Total cc. O_2 abs. (uncorr.)	Per cent. of total absorption after minutes 10	20	30	40	50	60
1	Ethyl MgBr	26	0.00645	66.5	25	38	53.7	63.4	79.5	87.2
2	Ethyl MgBr	26	.00645	75.5	34	54	69.5	85.1	95.9	98.1
3	Ethyl MgBr	29	.00516	56	23.2	46.4	60.7	82.1	91.1	93.4
4	Phenyl MgBr	28	,00602	51	24.5	38	54	65	71.6	80
5	Octyl MgBr	27	,00605	67	26.9	47.7	62.7	72.8	79.1	83.6

TABLE II

OXIDATION OF GRIGNARD REAGENT IN DIETHYL ETHER AT 0°

Grignard reagent used	RMgX mole	O_2 abs. 0°, 760 mm., cc.	Mole of O_2 per 1 mole of RMgX	Per cent. O_2 absorbed 3 min.	5 min.	10 min.
Slow Stirring						
C_2H_5MgBr	0.0054	53	0.876	80	93	100
C_2H_5MgBr	.0054	55	.909	81	93	100
C_2H_5MgBr	.0108	97	.801	78	94	100
C_2H_5MgBr	.0162	145	801	73	90	100
C_2H_5MgBr	.0113	108	.857	75.5	87	100[a]
C_2H_5MgBr	.0113	106	.840	71	87	100"
$C_6H_5CH_2MgBr$	.0078	91	1.04	81	94	100[b]
$C_6H_5CH_2MgBr$	.0078	89	1.02	78.5	90	100
n-$C_{16}H_{33}MgBr$	.0072	83	1.03	80	94	100"
n-$C_{16}H_{33}MgBr$	.0060	72	1.07	82	95	100[b]
Rapid Stirring						
C_2H_5MgBr	0.0054	53	0.876	90	100	...
C_2H_5MgBr	.0054	51	.843	90	99	100[d]
C_2H_5MgBr	.0054	51	.843	89	98	100
n-$C_8H_{17}MgBr$	.0077	78	.905	90	97	100[d]
n-$C_8H_{17}MgBr$	.0077	86	1.0	91	97	100[d]
$C_6H_5CH_2MgBr$	.0078	91	1.04	83	94	100"
n-C_4H_9MgCl	.0052	49	0.845	90	97	100[d]
n-C_4H_9MgCl	.0052	51	.879	88	97	100
n-$C_{16}H_{33}MgBr$	.0060	61	.908	97	100	...
n-$C_{16}H_{33}MgBr$	.0060	56	.833	97	100	...
n-$C_{16}H_{33}MgBr$	.0060	57	.848	91	97	100[b]
C_6H_5MgBr	.0060	46	.636	90	97	100[d]

[a] Air was used in these experiments in place of oxygen. [b] No oxygen absorbed after seven minutes. [c] No oxygen absorbed after eight minutes. [d] No oxygen absorbed after six minutes.

While no attempt was made to regulate this closely, the original temperature and the final temperature were the same.

The data are reported in Table I.

Oxidation at 0°.—The apparatus was essentially the same as before but was more carefully assembled and the reaction vessel in which the oxidation was carried out was equipped with a stirrer and surrounded by an ice-bath held at 0°. Again no elaborate thermostat was used but the temperature was controlled within the range of about 1°. The oxygen was taken from an ordinary tank of compressed gas and purified by passing successively through a concentrated solution of potassium hydroxide, a soda lime tower, a concentrated sulfuric acid wash bottle and a tube of anhydrite.

The data are given in Table II.

Preparation and Isolation of Alcohols. (a) n-Octyl Alcohol.—A solution containing 0.242 mole of n-octylmagnesium bromide in 200 cc. of ether was oxidized by bubbling pure dry oxygen through the solution, which was cooled in an ice-bath. After two hours the reaction mixture was poured into 300 cc. of water and 10 cc. of concentrated hydrochloric acid. The water solution was extracted with three 100-cc. portions of ether. The extract was evaporated on the steam-bath and distilled. Twenty-seven grams (0.21 mole) (85% of the theoretical amount) of octyl alcohol boiling at 195–198°, and entirely soluble in cold concentrated sulfuric acid, was recovered. The melting point of the phenyl urethan (72–73°) compared well with the melting point (74°) which has been reported for this derivative.[11]

(b) Cetyl Alcohol.—An ether solution containing 0.07 mole of cetylmagnesium bromide was oxidized for two hours, decomposed and taken up in ether as above. The ether was evaporated and the product distilled under reduced pressure. Ten grams (59% of the theoretical amount) of material, distilling at 150–190° (2 mm.), but melting at 45–48°, was recovered. This material showed no depression of melting point when mixed with known cetyl alcohol. As a residue from the vacuum distillation, 8 g. of dotriakontane, melting at 68° was recovered.

Summary

1. The rates of oxidation of certain Grignard reagents have been determined under various conditions.

2. At low temperatures (0°) where the vapor pressure of ether is not high enough to prevent free access of air to the solution the oxidation has been found to proceed at a very rapid rate and may become a serious side reaction in the use of the Grignard reagent.

3. n-Octyl- and cetylmagnesium bromides have been oxidized by dry oxygen to give good yields of the corresponding alcohols.

URBANA, ILLINOIS

RECEIVED NOVEMBER 7, 1932
PUBLISHED APRIL 6, 1933

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(11) Bouveault and Blanc, *Compt* rend., 136, 1676 (1903).

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

The Acetoacetic Ester Condensation. V. The Condensation of Higher Esters

BY REINHOLD R. BRIESE AND S. M. MCELVAIN

In an earlier paper[1] it was pointed out that ethyl α-propionylpropionate and ethyl a-butyrylbutyrate could be prepared in excellent yields through an acetoacetic ester condensation of ethyl propionate and ethyl butyrate. The essential feature of the procedure was the prevention of the reversal of the condensation, $2RCH_2COOC_2H_5 + NaOC_2H_5 \rightleftharpoons RCH_2C(ONa){=}C(R)COOC_2H_5 + 2C_2H_5OH$ by removal of the alcohol as it was formed in the reaction mixture. This was accomplished by periodic distillations of portions of the ester, which had been used in considerable excess in the reaction.

Because of the preparative value of this reaction, it seemed desirable to extend this study to the higher homologous esters. The present paper reports the results which were obtained with ethyl valerate, caproate, heptoate, caprylate, pelargonate, caprate, laurate and myristate.

Each of these esters was condensed smoothly by sodium ethoxide to the corresponding keto ester in yields of 74–84% of the theoretical. It was not necessary to use an excess of the ester to remove the alcohol formed in the reaction since the higher boiling points of these esters allowed for the direct distillation of the alcohol from the reaction mixture without any appreciable loss of ester. Ethyl a-lauryl-laurate and ethyl a-myristylmyristate are solids and were purified by crystallization. The other β-keto esters are liquids at ordinary temperatures and consequently were purified by distillation. It was noticed that in the distillation of the keto esters derived from ethyl pelargonate and ethyl caprate small amounts of the corresponding ketones, pelargonone and caprinone, were obtained. These ketones resulted, presumably, from the pyrolysis of some of the keto ester during distillation, since it was found that carbon dioxide, ethylene, and carbon monoxide were evolved when each of these two keto esters was heated (at atmospheric pressure) to the temperature at which it distilled under diminished pressure. The β-keto esters were characterized by (a) the amount of carbon dioxide evolved on hydrolysis,[2] (b) the ketone produced by hydrolysis and (c) ultimate analyses. The carbon dioxide content of ethyl a-pelargonylpelargonate and ethyl a-caprylcaprate shows that considerable ketone is present in each of them. They were not purified further and consequently not analyzed. However, both of these impure β-keto esters gave excellent yields of the corresponding ketones on hydrolysis.

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(1) McElvain, THIS JOURNAL, 61, 3124 (1929).

(2) Cope and McElvain, *ibid.*, 64, 4322 (1932).

TABLE I

YIELDS AND PROPERTIES OF β-KETO ESTERS, $RCH_2COCH(R)COOC_2H_5$, AND KETONES, RCH_2COCH_2R

	$RCH_2COCH(R)COOC_2H_5$										RCH_2COCH_2R	
							Calcd.		Found			
R is	Formula	Yields, %[a]	B. p. (mm.), or m. p., °C.	d^{25}_{25}	n^{25}_{D}	% CO_2	C	H	C	H	M. p., °C.[c]	Yield, %[d]
n-C_3H_7[e]	$C_{12}H_{22}O_3$	77	109–110 (5)	0.9330	1.4306	97.2	67.23	10.35	66.87	10.34	88 (22 mm.)[g]	72
n-C_4H_9	$C_{14}H_{26}O_3$	80	132–133 (5)	.9203	1.4351	97.0	69.36	10.82	69.00	10.77	14–15	81
n-C_5H_{11}[f]	$C_{16}H_{30}O_3$	78	147–148 (5)	.9107	1.4386	97.8	71.05	11.19	70.72	11.16	30–31	82
n-C_6H_{13}	$C_{18}H_{34}O_3$	84	173–175 (5)	.9047	1.4418	96.3	72.42	11.49	72.12	11.33	41–42	93
n-C_7H_{15}	$C_{20}H_{38}O_3$	74	195–200 (5)			91.9					52–53	93
n-C_8H_{17}	$C_{22}H_{42}O_3$	74	220–225 (5)			78.0					58–59	95
n-$C_{10}H_{21}$	$C_{26}H_{50}O_3$	79	28–29			96.3	76.38	12.10	76.00	12.11	68–69	98
n-$C_{12}H_{25}$	$C_{30}H_{58}O_3$	84	37–38			95.3	77.18	12.53	77.07	12.73	78–79	97

[a] These yields represent either distilled or recrystallized product.

[b] Obtained by hydrolysis of the keto ester.[2] Values above 95% are considered quantitative.

[c] The values reported in this column agree with those recorded in the literature for these ketones. The latter values are omitted for the sake of economy of space.

[d] Based on keto ester used.

[e] Reported by Israel, *Ann.*, **231**, 200 (1885), as having been obtained as a by-product in the reaction of sodium on ethyl propionate; however, the manner in which this compound was supposed to have been produced leaves considerable doubt in the minds of the authors as to its formation by such a reaction.

[f] Obtained by Hamonet, *Bull. soc. chim.*, [3] **2**, 339 (1889), through action of ferric chloride on oenanthyl chloride.

[g] Boiling point.

It should be emphasized that the extent to which the acetoacetic ester condensation of these higher esters takes place and the smoothness with which the resulting keto esters are hydrolyzed to the corresponding ketones make available an excellent method of preparation of higher ketones of the type, RCH_2COCH_2R.

The yields and properties of these β-keto esters and the corresponding ketones are summarized in Table I.

Experimental

Materials Used.—The esters which were used in the condensation were prepared by standard methods given in the literature and were thoroughly dried over anhydrous sodium sulfate and distilled before use. Sodium ethoxide was prepared from absolute alcohol and powdered sodium under dry ether.[3]

β-Keto Esters.—In a 125-cc. modified Claisen flask, with a fractionating side arm 35 cm. long, was placed 0.1 mole of the ester and 0.05 mole of sodium ethoxide. The reaction flask was attached to the receiving flask (which was not cooled) and this flask in turn was attached through a soda lime tower and a safety bottle to a manometer and a water pump. The safety bottle contained a stopcock which could be opened to the air and by which the pressure in the system could be regulated. The reaction flask was then heated carefully in an oil-bath to a temperature and under a pressure that caused a moderate, but not too vigorous, evolution of alcohol vapor as shown by the ebullition of the reaction mixture. The required temperature and pressure varied with the boiling point of the esters, the lower esters requiring lower reaction temperatures and higher pressures in order to prevent loss of ester. Consequently the time necessary for the completion of the reaction in these cases was increased. A summary of the conditions for the reaction of the various esters is given in Table II. Column 3 gives the temperatures and column 4 the pressures which were found to be most satisfactory at the beginning of each reaction to ensure a moderate evolution of alcohol. After the reaction had proceeded for some time these temperatures and pressures could be raised and lowered, respectively, without any appreciable loss of ester. Column 5 in Table II gives the time required for all of the alcohol to be evolved, *i. e.*, until the reaction mass ceased ebullition.

TABLE II

CONDITIONS AND TIME REQUIRED FOR FORMATION OF VARIOUS β-KETO ESTERS

Ester used, ethyl	B. p. of ester, °C. (mm.)	Reaction temp., °C.	Reaction pressure, mm.	Time for completion, hr.
Valerate	142–146 (750)	89–90	120–130	7–8
Caproate	57-60 (14)	90–95	75–80	7–8
Heptoate	75–79 (15)	90–95	60–65	7
Caprylate	94–99 (16)	90–95	20–25	5
Pelargonate	107–110 (15)	100–105	15–20	4–5
Caprate	118–121 (15)	105–110	15–20	4
Laurate	143–146 (15)	120–125	15–20	4
Myristate	167–170 (15)	125–130	15–20	4

The resulting reaction mixture was, at the temperature of reaction, a clear liquid with no visible particles of sodium ethoxide in suspension. The reaction products obtained from those esters above ethyl caprylate in molecular weight remained liquid after cooling to room temperature, but those derived from the lower molecular weight esters solidified to a clear, red transparent mass. The reaction product after cooling

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[3] Houben-Weyl, Vol. II, 1922, p. 578.

was treated with the calculated quantity of **30%** acetic acid and shaken vigorously until the sodium salt had been completely decomposed. The keto ester was then extracted with **25** cc. of benzene and the resulting benzene solution, after washing with water, was dried over anhydrous sodium sulfate. The benzene was removed from the keto ester by distillation. Ethyl a-lauryl-laurate and ethyl a-myristylmyristate were recrystallized from absolute methanol. The other keto esters, being liquids, were purified by distillation. This procedure was quite satisfactory for all of the esters except ethyl a-pelargonylpelargonate and ethyl a-caprylcaprate, both of which suffered a small amount of pyrolysis to the corresponding ketone, which appeared as a low boiling, solid fraction in the distillation. These particular keto esters when heated at atmospheric pressure to the temperature at which they boiled under diminished pressure slowly evolved ethylene, carbon dioxide and carbon monoxide.

The properties of these keto esters are summarized in Table I.

Hydrolysis of **the β-Keto** Esters to Ketones.—The keto esters were hydrolyzed by refluxing for three to four hours with a **5%** solution of potassium hydroxide in 90% alcohol. In the cases of valerone and caprone the alcohol was removed by distillation and the residue diluted with water, whereupon the liquid ketone layer separated. This was further purified by distillation. The higher ketones crystallized out from the alcoholic potassium hydroxide solution on cooling and after filtration were recrystallized from alcohol. The properties and yields of these ketones are listed in Table I.

Summary

The acetoacetic ester condensation has been applied to the synthesis of the following β-keto esters: ethyl a-valerylvalerate, ethyl α-caproylcaproate, ethyl a-heptoylheptoate, ethyl α-caprylylcaprylate, ethyl α-pelargonylpelargonate, ethyl a-caprylcaprate, ethyl a-lauryl-laurate, ethyl a-myristylmyristate.

Since these keto esters are readily hydrolyzed to the corresponding ketones, this procedure offers a most satisfactory method of preparation of the latter type of compounds.

MADISON, WISCONSIN

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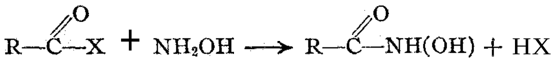
[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Molecular Rearrangements Involving Optically Active Radicals. III. The Lossen Rearrangement of Optically Active Hydroxamic Acids

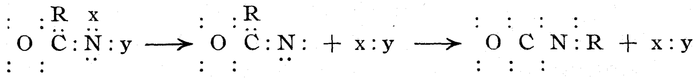
BY EVERETT S. WALLIS AND R. D. DRIPPS

The hydroxamic acids are crystalline compounds which may be prepared by the action of hydroxylamine on esters, acid anhydrides and acid chlorides



$$R-\overset{O}{\overset{/\!\!/}{C}}-X + NH_2OH \longrightarrow R-\overset{O}{\overset{/\!\!/}{C}}-NH(OH) + HX$$

It is a well-known fact that these substances and many of their derivatives are capable of molecular rearrangement. Lossen[1] first observed that the acetyl derivative of a hydroxamic acid when warmed with alkali produced an isocyanate. The metallic salts of these esters are very susceptible to this change. Of the several theories which have been advanced to explain the mechanism of this rearrangement the one which perhaps has received the most attention has been that of Stieglitz[2] which assumes the transient existence of an unstable univalent nitrogen compound. His investigations have made it evident that the Lossen, Curtius and Hofmann rearrangements are fundamentally alike, and he has proposed that all rearrangements of this character take place in a similar manner. In terms of modem valence conceptions Jones and Hurd[3] formulated this theory as follows



$$\underset{:}{\overset{:}{O}}\ \underset{:}{\overset{:R}{\ddot{C}}}:\underset{\cdot\cdot}{\overset{x}{\ddot{N}}}:y \longrightarrow \underset{:}{\overset{:}{O}}\ \underset{:}{\overset{:R}{\ddot{C}}}:\underset{\cdot\cdot}{N}: + x:y \longrightarrow \underset{:}{\overset{:}{O}}\ \underset{:}{\overset{:}{C}}\ \overset{:}{N}:R + x:y$$

and assumed that the relative ease of rearrangement depends not only upon the groups x and y, and the formation of the univalent nitrogen derivative, but also upon the nature of the radical, R; the greater the tendency of this radical to exist as a free radical the greater the ease of rearrangement. Many facts have been submitted by Jones and his coworkers[4] to support this hypothesis.

In carrying out certain of these investigations Jones and Wallis[5] studied the rearrangement of certain optically active acid azides and optically active hydroxamic acids in which R is an optically active radical. Their experiments with d-benzylmethylacetazide, $(C_7H_7)(CH_3)CHCON_3$, showed that this compound on rearrangement gave an optically active isocyanate

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(1) Lossen, Ann., 186, 1 (1877); 252, 170 (1889); 281, 169 (1894).

(2) Stieglitz, Am. Chem. J., 18, 751 (1896); *ibid.*, 29, 49 (1903); Stieglitz and Earle, *ibid.*, 30, 399, 412 (1903); Stieglitz and Slossen, Ber., 28, 3265 (1895); ibzd., 34, 1613 (1901); Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

(3) Jones and Hurd, Tars JOURNAL, 43, 2422 (1921).

(4) Jones and Hurd, *ibid*, 43, 2422 (1921); Jones and Root, *ibid*, 48, 181 (1926); Hurd, *ibid.*, 45, 1472 (1923).

(5) Jones and Wallis, *ibid*, 48, 169 (1926).

which could be converted by ammonia into an optically active monosubstituted urea, and by hydrolysis with concentrated hydrochloric acid into an optically active amine hydrochloride. These results established the fact that regardless of the actual mechanism[6] of this type of rearrangement, the radical, R, in its migration from the carbon atom to the nitrogen atom maintained an asymmetric configuration.

This conclusion has been further substantiated by Wallis and Nagel[7] in their studies on the rearrangement of optically active amides. When d-benzylmethylacetamide, $C_7H_7(CH_3)CHCONH_2$, was treated with a cold strongly alkaline solution of sodium hypobromite and the mixture warmed to 70–80° in order that rearrangement might take place, the amine so obtained in the form of its hydrochloride was found to be optically active. This fact makes it evident that in the Hofmann rearrangement of an optically active amide, as well as in the Curtius rearrangement of an optically active azide, the radical, R, during its migration from the carbon atom to the nitrogen atom, maintains its asymmetry.

However, in their investigations on the Lossen rearrangement of *d*-benzylmethylacethydroxamic acid, $C_7H_7(CH_3)CHCONHOH$, Jones and Wallis[6] found that the final product which they isolated gave no appreciable rotation. Three possible explanations of this apparent exception were offered. (1) In this rearrangement the radical, R, might actually racemize during its migration from the carbon atom to the nitrogen atom. (2) Inasmuch as the first product of the rearrangement, benzylmethylmethylisocyanate was not isolated as such but was converted by hydrolysis with water at 80–90° to the sym-di-benzylmethylmethyl urea, racemization might take place during this second stage of the reaction. **(3)** Since this symmetrically disubstituted urea was found not to be very soluble in the common organic solvents at room temperature and, therefore, available in solution only in small concentration, it would not be possible to obtain an appreciable polarimetric reading if the urea actually possessed a low specific rotation. Two experimental facts were observed which gave some indication of the true explanation. (a) The melting points of the urea prepared from the d, *l*, and dl forms of the hydroxamic acid were found to

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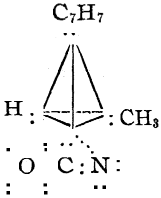
(6) It should be recalled that the nature of this migrating radical, R, has been considered as positive by Jones [Am. Chem. J., **50, 441** (1913)] and as negative by Stieglitz [THIS JOURNAL, 36, **280** (1914); **ibid., 38, 2047** (1916)] and more recently by Whitmore [ibid., 54, **3274, 3436** (1932)]. Jones and Wallis in their discussion of the results stated above pointed out, however, that another interpretation was possible, namely, "that the rearranging group does not exist as a free radical but that in some way, before the group actually parts company with its carbon neighbor, the univalent nitrogen atom has begun already to exercise its influence on the radical, in such a manner that when cleavage actually does take place, a change in the configuration of the groups about the asymmetric carbon atom is prevented." They stated that this influence could be imagined to be of the nature of a partial valence and they pictured the univalent nitrogen derivative on this assumption as indicated. This interpretation has recently received experimental support in this Laboratory and will be discussed in Part IV of this series of papers.



(7) Wallis and Nagel, THIS JOURNAL, **53, 2787 (1931).**

be the same. This would perhaps indicate that racemization at some stage in the process was the more plausible. (b) d-Benzylmethylmethylisocyanate prepared from the Curtius rearrangement of the d-acid azide gave on hydrolysis with water at 90° a urea of the same composition and melting point which showed no appreciable rotation. This makes it evident that it is unnecessary to assume that in the rearrangement of the hydroxamic acid derivative racemization takes place during the migration of the radical from the carbon atom to the nitrogen atom.

We have continued these investigations on the Lossen rearrangement of hydroxamic acids in order to determine more definitely the true nature of the first products of the rearrangement, and to see whether in this rearrangement as well as in the Hofmann and Curtius rearrangements the radical actually maintains an asymmetric configuration during its transfer from the carbon atom to the nitrogen atom. For this purpose we again prepared d-benzylmethylacethydroxamic acid in the form of its benzoyl derivative and converted it into its potassium salt by the method previously described by Jones and Wallis.[8] Rearrangement of this compound was carried out in such a manner as to enable us to obtain the isocyanate, first formed. A benzene solution of this isocyanate was found to be dextrorotatory. Ammonia gas reacted with the d-isocyanate to form the monosubstituted urea, $C_7H_7(CH_3)CHNHCONH_2$, a crystalline compound melting at 136.5–137°. Its specific rotation in acetone at 20° was found to be +10.1°.

Therefore it must be concluded that in the Lossen rearrangement of an optically active hydroxamic acid as well as in the Hofmann rearrangement of an acid amide, and the Curtius rearrangement of an acid azide, the radical actually maintains an asymmetric configuration during the rearrangement. The fact that the sym-di-benzylmethylmethyl urea, $C_7H_7(CH_3)CHNHCONHCH(CH_3)C_7H_7$, prepared by Jones and Wallis showed no appreciable rotation must be attributed to explanations 2 or 3 as stated above.

It is also to be noted that the value of the specific rotation of the monosubstituted urea prepared by the rearrangement of the hydroxamic acid derivative is of the same magnitude as the value of the specific rotation of the same urea prepared by rearrangement of the acid azide. A similar fact was observed by Wallis and Nagel[7] in their studies on the Hofmann rearrangement. The amine hydrochloride prepared from the acid azide, and from the acid amide, gave the same value for its rotatory power. They reasoned from their experiments that if partial inversion (racemization) took place, it could be detected inasmuch as the conditions of the rearrangement are very different. It is improbable that the amount of inversion would be the same. The above results on the monosubstituted

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(8) Jones and Wallis, THIS JOURNAL, *48*, 176 (1926).

urea justify with an added certainty their conclusions that in rearrangements of this type the radical, R, has either the same configuration as it had originally or that it undergoes complete inversion. Partial inversion seems unlikely. If we take into account the sign of the rotatory power perhaps the first conclusion is more probable.

Experimental Part

Preparation of the Benzoyl Ester of *d*-Benzylmethylacethydroxamic Acid, C_7H_7-$(CH_3)CHCONHOCOC_6H_5$.—This compound was prepared from d-benzylmethylacetic acid. The acid used in these experiments was prepared from ethyl acetoacetate according to the method of Conrad,[9] with a few modifications described by Jones and Wallis.6 It was resolved into its optically active isomers by the method of Kipping and Hunter.[10] Its rotation α_D at 20" without solvent in a 100-mm. tube was +20.12°. The methyl ester of this acid was prepared and converted into the hydroxamic acid according to the method of Jones and Wallis.[5] The benzoyl derivative was prepared according to the method of Jacobs and Heidelberger,[11] a modification of the Schotten–Baumann reaction. This ester melted at 115.5–116.5" after recrystallization from ethylacetate and petrolether (30–60°). 0.2079 g. of this compound dissolved in ethyl alcohol (95%), total volume 5.00 cc.. gave the following rotations at 20° in a 200-mm. semi-micro tube: $\alpha_{6563} = +4.95$; $\alpha_{5893} = +6.37$; $\alpha_{5463} = +7.68$; $\alpha_{4861} = +10.30$. $[\alpha]^{20}_{6563} = +59.5$; $[\alpha]^{20}_{5893} = +76.7$;[12] $[\alpha]^{20}_{5463} = +92.1$; $[\alpha]^{20}_{4861} = +120.2$.

Preparation of *d*-Benzylmethylmethyl Urea, $C_7H_7(CH_3)CHNHCONH_2$.—One gram of the d-benzoyl ester was converted into the potassium salt by the method described by Jones and Wallis.[8] The salt which precipitated as a white material was filtered quickly and suspended immediately in dry benzene. This suspension was refluxed for fifteen minutes on the water-bath and after cooling to room temperature was filtered. The residue, which was mostly potassium benzoate, was discarded. The benzene solution possessed a sharp penetrating odor characteristic of isocyanates and was dextrorotatory. Dry ammonia gas was bubbled through the solution for ten minutes and a white precipitate soon formed. The suspension was allowed to stand in the ice box for a short time and then filtered; yield 0.5 g. Recrystallization from alcohol and water gave a solid which melted at 136.5–137°. The melting point of *d*-benzylmethylmethyl urea as reported by Jones and Wallis was 136°. 0.0824 g. of this urea dissolved in pure acetone, total volume 5.00 cc., gave the following rotations at 20° in a 200-mm. semi-micro tube: $\alpha_{6563} = +0.26$; $\alpha_{5893} = +0.33$; $\alpha_{5463} = +0.40$; $\alpha_{4861} = +0.48$. $[\alpha]^{20}_{6563} = +7.9$; $[\alpha]^{20}_{5893} = +10.1$; $[\alpha]^{20}_{5463} = +12.1$; $[\alpha]^{20}_{4861} = +14.2$. The specific rotation $[\alpha]^{20}_{D}$ for the d-benzylmethylmethyl urea prepared from the d-acid azide and the isocyanate was reported by Jones and Wallis to be +10.7°.

Summary

Evidence is submitted in this paper to show that the Lossen rearrangement of an optically active hydroxamic acid yields an optically active rearrangement product. This result is similar to those previously communicated in this series of papers on the Hofmann rearrangement of an

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[9] Conrad and Bischoff, Ann., 204, 177 (1880); Conrad, *Ber.*, 11, 1055 (1878).

[10] Kipping and Hunter, J. *Chem. Soc.*, 83, 1005 (1903).

[11] Jacobs and Heidelberger, THIS JOURNAL, 39, 1441 (1917).

[12] The value of the specific rotation of this compound and the mixed levo form reported by Jones and Wallis in their experiments is not correct due to a clerical error. Their data should have read—a solution of 1 5400 g in alcohol, total volume 50 cc., gave a rotation of +4 40 in a 200 mm tube at 20°; $[\alpha]^{20}_{D} = +71.4$. This correction should be noted.

optically active amide, and the Curtius rearrangement of an optically active acid azide. The fact that optically active products were not obtained in the experiments described by Jones and Wallis on d-benzylmethylacethydroxamic acid is shown to be due to secondary causes and not to racemization of the compound during rearrangement.

d-Benzylmethylacethydroxamic acid in the form of its benzoyl ester was allowed to rearrange in such a manner as to enable us to study the first product of the rearrangement, benzylmethylmethylisocyanate, and to observe its behavior toward polarized light. A benzene solution of this compound was dextrorotatory. *d*-Benzylmethylmethyl urea was prepared from this isocyanate and its specific rotation was found to be of the same value as the urea prepared from d-benzylmethylacetazide.

These facts point to the conclusion stated in part II of this series that in rearrangements of this type the radical, R, has either the same configuration as it had before rearrangement or that it undergoes complete inversion during its migration from the carbon atom to the nitrogen atom. Partial inversion seems unlikely.

PRINCETON, NEW JERSEY

RECEIVED NOVEMBER 12, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Acenaphthene-*peri*-metathiazines and of Some Dyes Derived Therefrom[1]

BY MARSTON TAYLOR BOGERT AND RICHARD B. CONKLIN

Introductory

Having completed in these laboratories the synthesis of the naphthalene-*peri*-metathiazines[2] (I), we turned our attention to the analogously constituted and hitherto unknown acenaphthene-*peri*-metathiazines (11), and this contribution records their successful synthesis from the 4-nitroacenaphthene-3-sulfonchloride (IV). This synthesis supplies further corroboration of the constitution assigned to that nitrosulfo acid, as well as to those ascribed to the 3-nitro and 3-sulfo derivatives of acenaphthene.

The general plan of this synthesis involved the preparation of the 4-amino-3-acenaphthenylmercaptan (V) from the *peri*-nitrosulfonchloride (IV) and, by treatment of this *peri*-aminomercaptan with acid chlorides, effecting ring closure and thiazine formation, as described by Reissert,[3] and by Bogert and Bartlett,[2] in the naphthalene-*peri*-metathiazine group.

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(1) The completion of this work was made possible by a generous grant from the Trustees of the Joseph Henry Fund of the National Academy of Sciences, to whom we wish to express our gratitude.—M. T. B. and R. B C.

(2) Bogert and Bartlett, THIS JOURNAL, 53, 4046 (1931).

(3) Reissert, *Ber.*, 66, 858 (1922).

The flow sheet beyond exhibits diagrammatically the different steps carried out in this investigation.

The nitrosulfonchloride (IV) was reduced to the chlorostannate (VI), by the process developed by Bogert and Bartlett[2] in the naphthalene series, and this was used for the preparation of the desired acyl derivatives and thiazines, because it proved difficult and troublesome to obtain the aminomercaptan itself in satisfactory yield and purity. The acyl chlorides employed were benzoyl, m- and *p*-nitrobenzoyl.

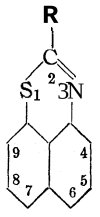
From the acylamino derivatives, the thiazines were obtained by digestion with a solution of fused sodium acetate in glacial acetic acid, a process of cyclization discovered by Bogert and Bartlett[2] in the naphthalene series. As in the latter series, so here this cyclization was accompanied with great increase in the depth of the color of the compounds and in their solubility in the solvents used.

The nitrophenylthiazines were readily reduced to the amines which, in turn, were sulfonated easily by concentrated sulfuric acid at 60–65°.

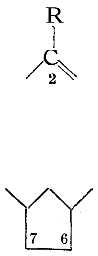
From the 2-(*m*-, and *p*-aminophenyl)-thiazines (X and XIII), dyes of Columbia Yellow (Chloramine Yellow) (Colour Index No. 814) type were prepared and their tinctorial properties compared with those of the similar dyes of the naphthalene series,[2] so as to learn what effect the presence of the ethylene bridge had upon these properties.

The dyeings on unmordanted unbleached cotton were not very different from the analogous naphthalene-*peri*-metathiazine dyes; that from the m-amino derivative gave a peach and from the p-isomer an apricot shade. In fastness to light and to bleeding, the dyes compared favorably with Columbia Yellow, but were less fast to laundering. Compared with the analogous naphthalene-peri-metathiazine dyes, they were equally fast to light and to laundering, and more stable to bleeding. They were not stable when left for some time in the presence of an excess of alkaline hypochlorite.

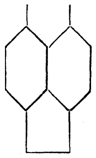
FLOW SHEET



(I). Naphthalene-*peri*-metathiazines

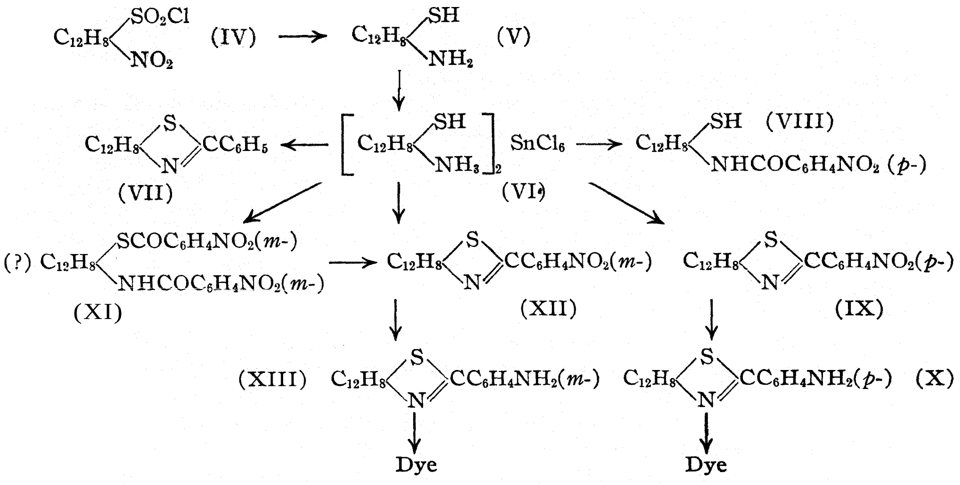


(II) Acenaphthene-*peri*-metathiazines



(III) $C_{12}H_8$

In the formulas below, the expression $C_{12}H_8$ is used to represent the complex (III) above.



Experimental

3-Amino-4-acenaphthenylmercaptan **Chlorostannate (VI)**.—This was prepared by a variation of the process employed by Bogert and Bartlett[2] in the naphthalene series, as follows. A suspension of 59 g. of powdered hydrated stannous chloride in 180 cc. of glacial acetic acid was brought into solution by passing in a current of dry hydrogen chloride. The increase in weight was about 20 g. generally, but if continued above an increase of 24 g. the reaction mixture tended to froth over when the nitrosulfonchloride was introduced. To this solution there was added, all at once, 10 g. of finely pulverized nitrosulfonchloride (IV) and the mixture was shaken vigorously. Solution ensued quickly, the temperature rose rapidly to about 80°, and the chlorostannate separated in fine yellow needles. When the mixture had cooled, the precipitate was filtered out, washed thoroughly with glacial acetic acid, dry benzene and finally with dry ether; yield, 11.5 g., or 93%. The product was soluble in absolute alcohol, but practically insoluble in chloroform, ether, ethyl acetate or benzene. Water decomposed it immediately.

For analysis, an analytically pure sample of the nitrosulfonchloride was treated with the carefully filtered reducing solution. The product was washed as described above and dried in a desiccator over sulfuric acid and paraffin.

Anal. Calcd. for $(HSC_{12}H_8NH_3)_2SnCl_6$: C, 39.14; H, 3.29; SnO_2, 20.48; Cl, 28.91; S, 8.72. Found: C, 39.40; H, 3.19; SnO_2, 20.34; Cl, 28.96; S, 8.70.

The product dissolved in glacial acetic acid–sodium acetate mixtures with precipitation of sodium chloride. In glacial acetic acid solution it reacted with acid chlorides, forming acyl derivatives of the *peri*-aminomercaptan and *peri*-metathiazines.

Di(*m*-nitrobenzoyl) Derivative of 3-Amino-4-acenaphthenylmercaptan (XI).—The chlorostannate (5 g.) was decomposed by heating it at 90° with 5 g. of fused sodium acetate in 100 cc. of glacial acetic acid, and the resultant mixture was treated at 60" with 6 g. of m-nitrobenzoyl chloride added all at once; yield of crude product, 59%. Recrystallized from glacial acetic acid and decolorized, it formed long fine yellow needles, insoluble in concentrated hydrochloric acid or in sodium hydroxide solution. In concentrated sulfuric acid it dissolved to a yellow solution, from which it was reprecipitated by dilution. In hot alcohol it was practically insoluble, but dissolved in hot ethyl acetate or in acetone. When placed in a bath at 233° (corr.), it began to turn pink immediately and decomposed completely at about 235.5° (con.)

Anal. Calcd. for $C_{26}H_{17}O_6N_3S$: C, 62.50; H, 3.43. Found: C, 62.67; H, 3.57.

When these experimental details were followed accurately, practically no thiazine (XII) was formed and there was no difficulty experienced in purifying the crude product as stated. Higher temperatures during the reaction gave appreciable amounts of the thiazine and variation of the other conditions likewise resulted in a product which could not be purified by crystallization from acetic acid.

3-*p*-Nitrobenzoylamino-4-acenaphthenylmercaptan (VIII).—Five grams of the chlorostannate was decomposed by heating it at 90° with a solution of 5 g. of fused sodium acetate in 50 cc. of glacial acetic acid. The resultant mixture was treated with 3.7 g. of powdered *p*-nitrobenzoyl chloride, added all at once, and the whole was shaken vigorously, refluxed for two hours and cooled. The precipitate was removed, washed with a little acetic acid and with water, and extracted with hot ethyl acetate (100 cc.) until the red color was removed. The insoluble portion (1.1 g.) was recrystallized from cellosolve and decolorized, when it formed pale brown microscopic needles which, when inserted in the bath at 245° (corr.), decomposed at 246–247° (corr.), turning dark red. The product was insoluble in sodium hydroxide solution or in concentrated hydrochloric acid. It dissolved in concentrated sulfuric acid to a yellow solution, from which it was reprecipitated by dilution with water. It was but slightly soluble in hot ethyl acetate, but in the presence of the thiazine dissolved sufficiently to render the isolation of the pure thiazine troublesome. In hot glacial acetic acid, it was but slightly soluble.

Anal. Calcd. for $C_{19}H_{14}O_3N_2S$: C, 65.11; H, 4.03; N, 7.82. Found: C, 65.51; H, 3.94; N, 8.07.

The thiazine also was formed in this reaction. Its preparation is described beyond.

2-Phenylacenaphthene-peri-metathiazine (VII).—To a solution of 5 g. of anhydrous sodium acetate in 50 cc. of glacial acetic acid at 90°, there was added 5 g. of the chlorostannate and the mixture was shaken at this temperature until all of the chlorostannate was decomposed (about ten minutes) and a clear orange solution resulted with precipitation of sodium chloride. Below 90°, this decomposition of the chlorostannate proceeded very slowly. A solution of 3 g. of benzoyl chloride in a few cc. of glacial acetic acid was then added all at once, the mixture was well shaken, allowed to stand for an hour, refluxed for an hour and a half and permitted to cool. The precipitate was removed, washed with a little acetic acid, then with water. There remained 0.5 g. of red needles, m. p. 105° (corr.). The red filtrate, poured into water, separated an orange precipitate which was collected and dried, and contained considerable tin. The combined precipitates were extracted with alcohol until the red color was completely removed. As the alcohol extract cooled, 1.1 g. of long feathery red crystals were deposited, m. p. 122–123° (corr.). By repeated crystallization and decolorizing in alcoholic solution, this changed to reddish-orange needles, which began to shrink and soften at about 128° and melted completely at 142.3° (corr.). The compound was easily soluble in alcohol, acetone, ethyl acetate or benzene.

Anal. Calcd. for $C_{19}H_{13}NS$: C, 79.39; H, 4.56; N, 4.88. Found: C, 79.45, 79.49; H, 5.25, 5.27; N, 5.22.

2-*m*-Nitrophenylacenaphthene-*peri*-metathiazine (XII).—When 5 g. of the di-(m-nitrobenzoyl) derivative (XI) was refluxed with a solution of 20 g. of fused sodium acetate in 200 cc. of glacial acetic acid, it dissolved within five minutes, forming a deep orange-red solution. The refluxing was continued for some forty minutes longer and the solution was then allowed to cool. The thiazine which separated was removed, washed with a little water, crystallized and decolorized in acetone solution; yield, 2 g. or 60%. It formed orange-red long glistening flat needles which, when placed in the bath at 183° (corr.), shrank at about 189° and melted with decomposition at 190.3–191.3° (corr.). The compound was freely soluble in ethyl acetate, glacial acetic acid or acetone, but only slightly in alcohol, *Anal.* Calcd. for $C_{19}H_{12}O_2N_2S$: C, 68.63; H, 3.64; N, 8.44. Found: C, 68.72; H, 3.74; N, 8.59.

2-*p*-Nitrophenylacenaphthene-*peri*-metathiazine (1x1.—This thiazine was formed during the production of the p-nitrobenzoyl mercaptan (VIII), but its isolation proved troublesome. It was found in the original acetic acid–sodium acetate solution, in the ethyl acetate extracts and the cellosolve mother liquors. Dilution of the original acetic acid–sodium acetate mother liquor with water gave a chocolate precipitate containing considerable tin. The ethyl acetate extracts, containing some precipitate, were cooled and yielded 1.1 g. of greenish solid, melting with decomposition at about 232". The ethyl acetate filtrate from this was used to extract the chocolate precipitate from the acetic acid–sodium acetate solution, and in this way 0.25 g. more of crude thiazine was recovered. Finally, concentration of the cellosolve mother liquors gave about 0.3 g. of purer thiazine. These three lots of crude thiazine were combined and extracted repeatedly by refluxing with ethyl acetate. The thiazine thus isolated (1.1 g.) was purified by further crystallization and decolorizing in ethyl acetate, and then appeared in long lustrous needles, almost black in color, moderately soluble in hot glacial acetic acid, but only slightly soluble in hot alcohol. Its solutions were dark red. Placed in the bath at 244° (corr.), it decomposed at 253.7° (corr.).

Anal. Calcd. for $C_{19}H_{12}O_2N_2S$: C, 68.63; H, 3.64; N, 8.44. Found: C, 68.80; H, 3.55; N, 8.38.

It was prepared by decomposing 5 g. of the chlorostannate at 90° with 100 cc. of glacial acetic acid and 5 g. of fused sodium acetate, then treating this at 60° with 6 g. of p-nitrobenzoyl chloride, added in one lot. When the reaction was completed, the mixture was allowed to cool, the precipitate was removed, washed with acetic acid and with water, and then refluxed for three hours with 200 cc. of glacial acetic acid containing 20 g. of fused sodium acetate; yield, 2.25 *g.* of greenish black crystals of the thiazine, which melted with decomposition at about 243° (corr.), and were sufficiently pure for reduction to the corresponding amine (X).

2-m-Aminophenylacenaphthene-peri-metathiaze (XIII).—The corresponding nitro derivative (XII) (2 g.) was refluxed for two hours with a solution of hydrated stannous chloride (5.5 g.) in a mixture of alcohol (200 cc.) and concentrated hydrochloric acid (12 cc.). The deep red solution was poured into water, sodium hydroxide added to alkaline reaction, the mixture left for thirty minutes at room temperature, the precipitate removed, washed, dried, extracted with hot alcohol, the alcohol extracts decolorized and filtered. Water was added to the hot filtrate until incipient clouding, when it was permitted to cool. The separated amine (yield, 1.2 g., or 66%), recrystallized from alcohol and water in a similar manner, formed orange-yellow needles, soluble in methyl alcohol, acetone, ethyl acetate or benzene; slightly soluble in concentrated hydrochloric acid to a pale violet solution; but dissolving in concentrated sulfuric acid to a deep violet, changing gradually to a potassium permanganate color and then to shades of red, from which it was partially reprecipitated by the addition of water. When placed in the bath at 165° (corr.), it darkened and melted with decomposition at 176.7–177.7° (corr.).

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.45; H, 4.67. Found: C, 75.03; H. 4.78.

2-*p*-Aminophenylacenaphthene-*peri*-metathiazine (X) was prepared by reduction of the nitro derivative (IX) in much the same way as the m-isomer, except that some mossy tin was added to assist the reduction and three times the volume of alcohol was found necessary. The yield of crude arnine was 72%, and the product formed orange needles which, when placed in the bath at 208° (corr.), gradually darkened and melted with decomposition at 214.8–215.8' (corr.). It was soluble in methyl alcohol, acetone. ethyl acetate or benzene. Its behavior with concentrated hydrochloric acid, or concentrated sulfuric acid, was the same as that of the m-isomer.

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.45; H, 4.67; S, 10.61. Found: C, 75.26; H, 4.36; S, 10.75.

Dyes of Columbia Yellow (Colour Index No. 814) Type from m- and *p*-Aminophenylacenaphthene-*peri*-metathiazines. From the m-Isomer.—When 1 g. of the amine was added to 30 cc. of concentrated sulfuric acid, it formed a solution of deep potassium permanganate color, which gradually changed to a deep wine red when the solution was heated for ten minutes at 60–65°. After cooling, the solution was poured upon ice, the flocculent orange precipitate collected, washed, dissolved in hot dilute sodium carbonate solution (leaving no insoluble residue), the hot solution acidified with hydrochloric acid, allowed to cool, the precipitate removed, washed and dried; yield, 1.3 g. of dark brown powder. This was dissolved in 250 cc. of hot very dilute sodium hydroxide, the solution cooled to room temperature, 3 cc. of 1.23 *N* sodium hypochlorite solution added and the mixture left for five hours at room temperature. It was then heated and an equal volume of hot filtered saturated salt solution added. The dye separated as a dark brown flocculent precipitate, which was filtered out when the solution was cold, dissolved in hot water, the solution filtered, the dye salted out again from the filtrate, washed with alcohol, ether and dried. It was insoluble in concentrated sodium hydroxide solution. In concentrated sulfuric acid, it dissolved with production of a port wine color. On prolonged contact with excess of alkaline hypochlorite, it was bleached to a pale yellow color, with marked increase in weight and loss of solubility in water.

The dyeings were carried out with 50 cc. of 0.1% dye solution, 2.5 g. of unbleached cotton, 62 cc. of water, ten drops of a 10% sodium carbonate solution and 37 cc. of a 1% sodium chloride solution, the mixture being heated for thirty minutes just below the boiling point.

Unmordanted unbleached cotton was thus dyed a peach shade, fast to light and bleeding, but only moderately fast to laundering.

From the *p*-Isomer.—The process was the same as for the m-isomer, varying only in some of the details.

The solution of the amine in the sulfuric acid, which was of potassium permanganate color at first, changed to a deep crimson red when heated. The crude aminosulfo acid was henna-colored when wet, but dark brown when dry; yield, 1.3 g. from 1 g. of the amine. The dye itself was a brown powder, slightly darker in color than its m-isomer, and in most of its physical, chemical and tinctorial properties resembled the latter, except that its dyeings on unbleached unmordanted cotton were of an apricot shade.

Summary

1. The synthesis of acenaphthene-*peri*-metathiazines has been accomplished, using 4-nitroacenaphthene-3-sulfonchloride as initial material, and their properties are described.

2. From the m- and *p*-aminophenylacenaphthene-*peri*-metathiazines dyes of Columbia Yellow (Colour Index No. 814) type have been prepared and their tinctorial properties recorded.

3. In preparation and properties, these metathiazines parallel closely the analogously constituted *peri*-metathiazines of the naphthalene series recently synthesized by Bogert and Bartlett.[2]

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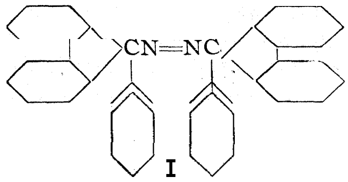
Some Reactions of Hydrazophenylfluorene

BY LOUIS A. PINCK

As part of a program of research on the organic chemistry of nitrogen it was desired to determine more fully the properties of a few symmetrical azotriarylmethanes. It has been shown by Wieland[1] that azotriphenylmethane, $(C_6H_5)_3CN{=}NC(C_6H_5)_3$, is extremely unstable, decomposing into triphenylmethyl and nitrogen. On that basis it might be assumed that similar symmetrical azotriarylmethanes would likewise be unstable. The present investigation was undertaken with the object of attempting the preparation of azophenylfluorene, I, by the oxidation of the corresponding hydrazo compound. This paper will deal principally with the preparation and reactions of hydrazophenylfluorene.


I

A series of preliminary oxidation experiments, first carried out with hydrazotriphenylmethane, consisted largely of a repetition of the work reported by Wieland. His observation concerning the probable transitory existence of azotriphenylmethane was confirmed. It was found, for example, that the halogens, bromine and iodine, reacted with hydrazotriphenylmethane even at −40°. The ultimate products identified were nitrogen, triphenylmethyl peroxide, triphenylmethyl halide, triphenylcarbinol and hydrazine hydrohalide.[2] In this study no greater success was achieved from attempts to oxidize hydrazotriphenylmethane with freshly prepared oxides of silver, lead,[3] mercury and manganese. The action of benzoyl peroxide and benzoyl hydroperoxide upon the hydrazo compound yielded nitrogen and triphenylmethyl peroxide. Hydrazotriphenylmethane was decomposed by iodine pentoxide with the evolution of nitrogen and the simultaneous liberation of iodine.

It was considered that the extreme instability of azotriphenylmethane was intimately related to the weak affinity of the substituent triphenylmethyl group, which is manifested by the ability of the latter to exist as a free radical. In making another choice for the synthesis of a compound of

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[1] Wieland, *Ber.*, **42**, 3020 (1909). See also Stieglitz and Brown, THIS JOURNAL, 44, 1270 (1922).

[2] Wieland reported the formation of hydrazotriphenylmethane hydrochloride from the hydrazo compound and hydrogen chloride. Upon repeating this experiment it was found that the reaction yielded triphenylchloromethane and hydrazine hydrochloride.

$$(C_6H_5)_3CNHNHC(C_6H_5)_3 + 3HCl \longrightarrow 2(C_6H_5)_3CCl + N_2H_4{\cdot}HCl$$

This reaction was found to be useful in the identification of a mixture of hydrazotriphenylmethane and triphenylmethyl peroxide.

[3] The use of silver and lead oxides was a repetition of Wieland's work and his results were confirmed.

the azotriarylmethane type, azophenylfluorene was selected. This compound seemed to be somewhat more promising because the related hydrocarbon, dibiphenylenediphenylethane, is reported to be dissociated to a less extent than hexaphenylethane.[4] Furthermore, the derivatives of phenylfluorene are much more stable and in general react more sluggishly than the corresponding derivatives of triphenylmethane. For example, Kliegl[5] pointed out that halogen derivatives of phenylfluorene appeared to be unusually stable when digested with water. He also reported his inability to secure condensations between the carbinol with aniline, hydroxylamine and phenylhydrazine similar to the well-known condensations of triphenylcarbinol that were first carried out by Baeyer and Villiger.[6] It is of interest, in this connection, that the chloride and carbinol derived from triphenylmethane are much more easily and smoothly reduced by various reagents to the parent hydrocarbon than the corresponding derivatives of phenylfluorene.[7]

Hydrazophenylfluorene was synthesized by the reaction of hydrazine hydrate with phenylbromofluorenein xylene solution. In various attempts to convert the product to the corresponding azo compound the following reagents were tried: "active" silver oxide,[8] potassium permanganate, benzoyl peroxide, bromine and palladium black. In the experiment with silver oxide practically all of the hydrazo compound was recovered. With potassium permanganate in anhydrous acetone and with benzoyl peroxide hydrazophenylfluorene was oxidized to phenylfluoryl peroxide. Better control of the oxidation did not result when bromine was employed.

Wieland's work[9] on the use of palladium black as catalyst for oxidation and reduction suggested the possibility that this reagent might cause the dehydrogenation of hydrazophenylfluorene, with the formation of the corresponding azo compound as one of the products. The results of the present investigation indicated that palladium black did promote the dehydrogenation of hydrazophenylfluorene. The principal products were nitrogen, phenylfluroene and a relatively small amount of dibiphenylenediphenylethane. It is not improbable that azophenylfluorene was an intermediate product. Its formation might be followed by its thermal decomposition and the subsequent hydrogenation of some of the resulting phenylfluoryl to phenylfluorene in the presence of palladium.

The action of oxygen upon hydrazophenylfluorene in the presence of palladium was studied. The hydrazo compound was oxidized, yielding a mixture of phenylfluoryl peroxide and phenylfluorenol. No other product could be isolated. The action of hydrogen in the presence of palladium

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(4) Schlenk, Herzenstein and Weickel, *Ber.*, 43, 1754 (1910).

(5) Kliegl, *ibid.*, 38, 284 (1905).

(6) Baeyer and Villiger, *ibid.*, 35, 3015 (1902).

(7) Unpublished work.

(8) Willstatter and Müller, *Ber.*, 41, 2580 (1908).

(9) Wieland, *ibid.*, 45, 484, 2606, 2615 (1912): 46, 2085, 3327 (1913).

black upon phenylfluoryl peroxide yielded phenylfluorene. A similar result has been noted for triphenylmethyl peroxide.[10]

Experimental

Preparation of **Hydrazotriphenylmethane.**—The following procedure is similar to the methods previously reported by Wieland and Stieglitz and Brown but is more convenient and results in higher yields. To a solution of 30 g. of 90% hydrazine hydrate in about 100 cc. of dry pyridine, 114 g. of triphenylchloromethane was added in small portions so that the temperature of the reaction mixture did not rise above 45–50°. The solution was agitated during the addition of the halide and for an hour thereafter. The solid organic matter was precipitated by the dilution of the reaction mixture with a large volume of water, collected and then extracted with alcohol, which dissolved triphenylcarbinol and left the hydrazotriphenylmethane. The latter was then crystallized and recrystallized from a mixture of benzene and alcohol as recommended by Wieland; yield 66 5 g., m. p. 212° with decomposition.

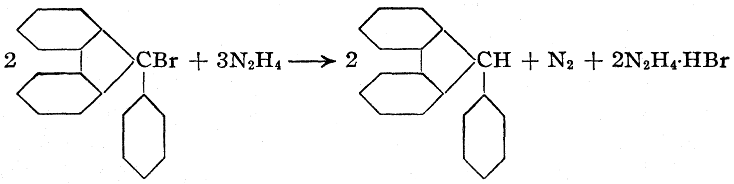
Preparation of **Hydrazophenylfluorene.**[11]—A mixture of 15 g. of phenylbromofluorene and 7.5 cc. of hydrazine hydrate (90%) in 50 cc. of xylene was heated at 100° for about two hours. The excess hydrazine was separated from the supernatant xylene solution and the latter diluted with petroleum ether and cooled in an ice-bath. A white solid (4.1 g.) precipitated; m. p. 181–182° with decomposition. This product was identified as a mixture of hydrazophenylfluorene and phenylfluoryl peroxide. The mixture was treated with warm ether, in which the hydrazo compound is considerably more soluble than the peroxide. Separation was thus effected. The hydrazo compound was recovered from the ether solution and upon recrystallization from the same solvent a yield of but 2 g. was obtained; m. p. 195–196°, with decomposition. The identification of the residual phenylfluoryl peroxide is detailed below.

Anal. Calcd. for $C_{38}H_{28}N_2$: C, 89.02; H, 5.51; N, 5.47. Found: C, 88.69, 88.77; H, 5.25, 5.34; N, 5.47, 5.55.

Hydrazophenylfluorene is very soluble in chloroform, xylene, acetone and benzene, somewhat soluble in alcohol and ether, and less soluble in petroleum ether, and acetic acid. This compound is much more susceptible to oxidation by air than hydrazotriphenylmethane, and, unlike the latter, does not react readily with ethereal or aqueous hydrogen chloride.

The ether insoluble fraction after two recrystallizations from benzene melted at 194°, and its melting point was not depressed after mixing with phenylfluoryl peroxide. Upon concentration of the mother liquor (xylene and petroleum ether solution) a crop of 3.5 g. of phenylfluorene, m. p. 146°, was obtained; mixed m. p. with phenylfluorene, 147".

When the reaction was carried out at room temperature, the chief product was phenylfluorene.



A solution of 2 g. of phenylbromofluorene, 1 cc. of hydrazine hydrate (90%) in 20 cc. of xylene was allowed to stand at room temperature for about a week. Gas was slowly

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[10] Wieland and Müller, Ann., 401, 233 (1913)

[11] This compound can also be advantageously prepared by the use of acetonitrile as the solvent (unpublished work).

evolved and a small deposit of needle-like crystals was formed. The xylene solution was pipetted from the hydrazine hydrate and concentrated to a small volume; alcohol was added and crystallization induced, whereupon 0.70 g. of white solid separated; m. p. 144–145°. This was recrystallized from alcohol and ether; m. p. 147°; mixed m. p, with phenylfluorene, 147".

Action of Sodium upon Hydrazophenylfluorene.—It had been observed that hydrazotriphenylmethane dissolved in liquid ammonia reacts at 0° with sodium; the product after treatment of the reaction mixture with water is triphenylmethane in 90% yield.[12]

A similar reaction was observed with hydrazophenylfluorene. A solution of 0.162 g. of hydrazophenylfluorene with an excess of sodium (0.029 g.) in dry liquid ammonia reacted vigorously at 0°, forming an orange colored solid (sodium phenylfluorene?). This was treated with water, and 0.150 g. of a white hydrolysis product was obtained; m. p.. 143° After one recrystallization from alcohol its melting point was 147° and was not depressed when the substance was mixed with phenylfluorene.

Attempts to Prepare Azophenylfluorene by the Oxidation of Hydrazophenylfluorene.—Four-tenths gram of hydrazophenylfluorene, 0.05 g. potassium permanganate and several grams of preheated sodium sulfate were added to acetone which had been purified by four distillations in the presence of potassium permanganate and dried over potassium hydroxide. The reaction mixture was shaken for four hours until all of the permanganate had been brought into reaction. The solution was filtered and concentrated in a vacuum desiccator. The first crop of crystals were white in the presence of the solvent and turned pink when dry. a property characteristic of phenylfluoryl peroxide; m. p. 189°, and m. p. of a mixture with phenylfluoryl peroxide, 192° The residual material was found to consist of a mixture of hydrazophenylfluorene and phenylfluoryl peroxide.

A solution of 0.100 g. of benzoyl peroxide and 0.212 g. of hydrazophenylfluorene in 15 cc. of benzene was allowed to stand in a glass-stoppered Erlenmeyer flask in the dark for several weeks. Crystals were formed which upon filtration turned pink and melted at 192–193°. The melting point of a mixture with phenylfluoryl peroxide was also 192–193".

When a gas-evolution tube containing 0.1 g. of hydrazophenylfluorene in about 10 cc. of xylene was heated in a water-bath to 80°, a slow evolution of a gas resulted. Another tube (Pyrex glass) containing a similar solution was placed in direct sunlight (temperature, 8°). Within two hours the solution turned yellow and gas was slowly given off. From a third tube kept in the dark for two weeks, less than 0.1 cc. of gas was obtained. After a specimen of the pure, solid hydrazo compound had been stored in a stoppered bottle in the dark for three to four months, it was re-analyzed; the nitrogen content (Dumas) was found to be 4.0%. representing a loss of 1.5%

Behavior of Hydrazophenylfluorene in the Presence of Palladium Black.—Palladium black was prepared according to the directions given by Wieland.[13] In order to remove occluded oxygen from the palladium, the latter was treated with a stream of hydrogen for half an hour at room temperature and then for an hour at 100°. It was found that such treatment did not reduce the activity of the catalyst. One-tenth gram samples of hydrazophenylfluorene in 10 cc. of benzene (sodium-dried) and quantities varying from 0.2 g. to 0.8 g. of palladium black were used in each experiment. The air over the benzene solution was displaced by nitrogen in the presence of which the palladium was added. The tubes containing the reaction mixture were cooled in a liquid ammonia bath, evacuated, sealed and removed from the bath. A fairly vigorous gas evolution was observed for a period ranging from one to two hours. In a "blank run"

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(12) Unpublished work.

(13) Wieland, *Ber.*, **45**, 484 (1912).

with palladium black and benzene there was no perceptible gas evolution. In order to decrease the rate of decomposition, ether was substituted for benzene in one experiment and the observation was made at −48°. Here, too, gas was evolved. It was observed that the reactions did not go to completion, even when they were carried out at a higher temperature for several days or when a second addition of fresh palladium was made.

The contents of a tube which had been shaken at room temperature for three to four hours were filtered in an atmosphere of nitrogen. The solvent was evaporated in a stream of nitrogen, leaving a residue which melted and decomposed over the range 130 to 185'. It was extracted with petroleum ether (b. p. 35 to 55°) and the material (0.070 g.) recovered by evaporation of the petroleum ether was recrystallized from ligroin (b. p. 90 to 120"); m. p. 142"; mixed m. p. with phenylfluorene, 144–145". The portion insoluble in petroleum ether melted and decomposed over the range 185 to 212° This behavior is similar to that of a mixture of hydrazophenylfluorene and dibiphenylenediphenylethane. Since dibiphenylenediphenylethane is rather rapidly converted to the corresponding peroxide upon exposure to air, the petroleum ether insoluble portion was allowed to stand exposed to air for twenty-four hours. It was then found to melt with decomposition at 185"; mixed m. p. with known phenylfluoryl peroxide 189°, mixed m p. with known hydrazophenylfluorene, 188–189°. A known mixture of hydrazophenylfluorene and phenylfluoryl peroxide (1:1) melted with decomposition at 189". The gas evolved in the reaction of hydrazophenylfluorene with palladium black was freed from benzene vapor in a special gas analysis apparatus and was found to consist of nitrogen.

Action of Oxygen upon Hydrazophenylfluorene in the Presence of Palladium Black.—To a solution of 0.1 g. of hydrazophenylfluorene in 10 cc. of benzene, 0.5 g. of palladium black was added, and air was bubbled through the solution for three hours at room temperature The solution was filtered and the solvent evaporated. The residue was washed with petroleum ether; m. p. 189–190°, with the characteristic orange-red coloration given by phenylfluoryl peroxide; mixed m. p. with the peroxide, 193°. The petroleum ether washings were evaporated and a substance was obtained which melted at 109°; mixed m. p. with phenylfluorenol, 109'.

Action of Hydrogen and Palladium Black upon Dibiphenylenediphenylethane.—Some of the ethane derivative, dissolved in benzene, was treated with hydrogen in the presence of palladium black for six hours at room temperature. The solution was filtered and the benzene evaporated in a stream of nitrogen. The residue melted at 142–143"; mixed m. p. with phenylfluorene, 145–146°.

Action of Hydrogen upon Phenylfluoryl Peroxide in the Presence of Palladium Black.—To a solution of 0.1 g. of phenylfluoryl peroxide in benzene was added some palladium black and the solution was treated with hydrogen at room temperature for three hours. The solvent was evaporated and the residue was found to melt at 180–182". It was extracted with petroleum ether. The insoluble portion melted at 194–195° (unchanged phenylfluoryl peroxide) and the fraction recovered by evaporation of the petroleum ether melted at 145°; mixed m. p. with phenylfluorene, 145°.

The author is indebted to a number of his colleagues for helpful suggestions and especially to Dr. Leslie Hellerman of the Johns Hopkins University for advice and encouragement.

Summary

1. Wieland's observation concerning the momentary existence of azotriphenylmethane was confirmed.
2. Hydrazophenylfluorene was synthesized by the action of hydrazine

hydrate upon phenylbromofluorene. With sodium in liquid ammonia solution, the hydrazo compound reacted to form a product, which, when hydrolyzed, yielded phenylfluorene. With various oxidizing agents, hydrazophenylfluorene yielded mainly phenylfluoryl peroxide.

3. In experiments with palladium black, evidence was obtained for the possible momentary existence of azophenylfluorene; the compound, if formed, decomposed under the experimental conditions yielding nitrogen, phenylfluorene and dibiphenylenediphenylethane. The action of oxygen upon hydrazophenylfluorene in the presence of palladium black led to the formation of phenylfluoryl peroxide and phenylfluorenol.

4. The action of hydrogen upon dibiphenylenediphenylethane and upon phenylfluoryl peroxide in the presence of palladium black yielded phenylfluorene.

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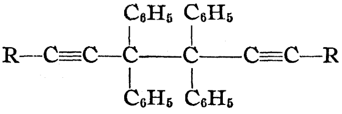
Rearrangements of Polyines. IV. Tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane

BY J. HARMON AND C. S. MARVEL

Acetylenic hydrocarbons of the type represented in formula I have been found to be quite unstable and to undergo a characteristic rearrangement to produce more stable isomeric hydrocarbons.[1] The nature of this rearrangement is still unknown and as yet it is impossible to assign definite structures to the stable hydrocarbons. The present communication describes another unstable hydrocarbon of type I and its rearrangement products.



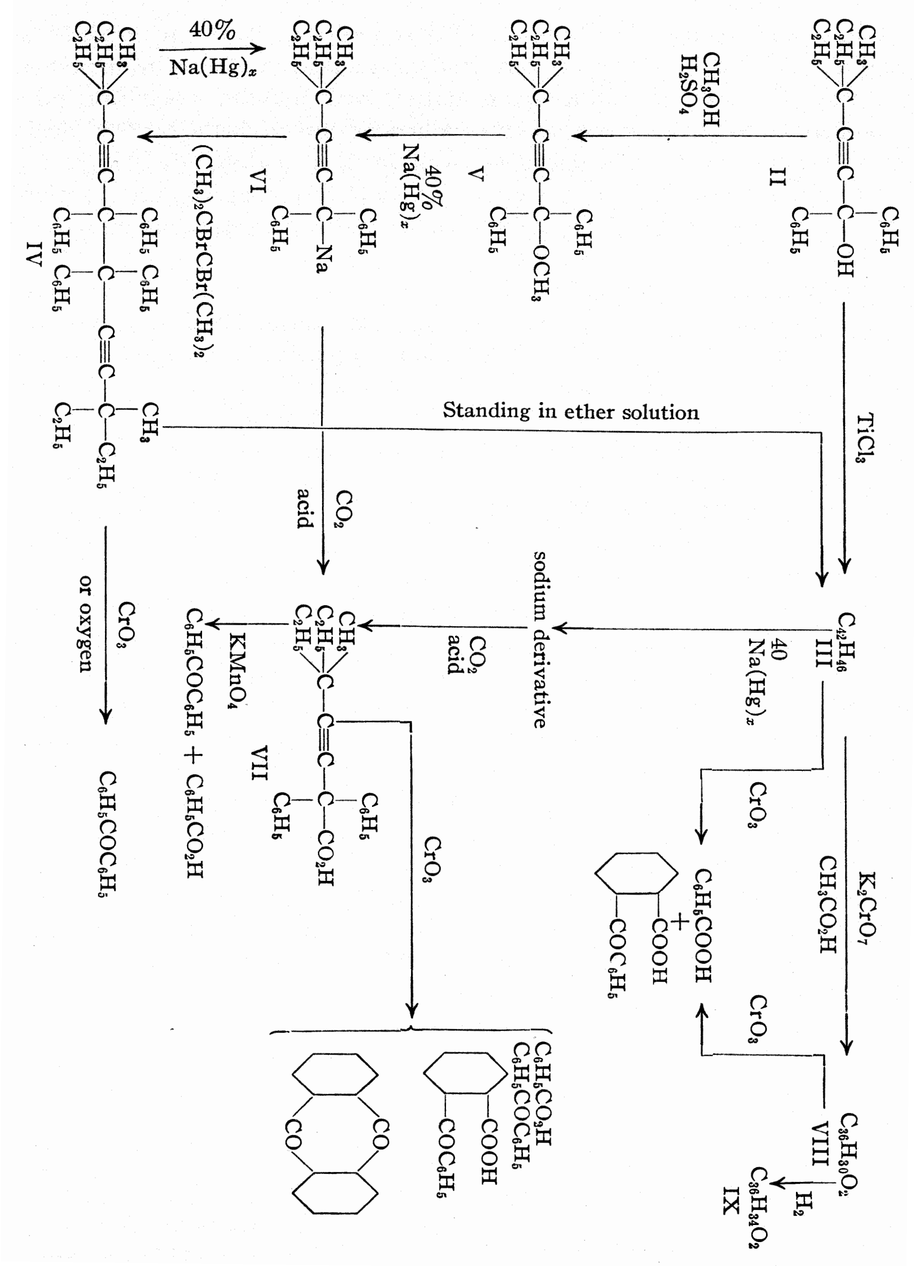
$$\begin{array}{ccccccc} & & C_6H_5 & & C_6H_5 & & \\ & & | & & | & & \\ R—C\equiv C & — & C & — & C & — & C\equiv C—R \\ & & | & & | & & \\ & & C_6H_5 & & C_6H_5 & & \end{array}$$

I

The reduction of diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol (II) with titanium trichloride to give the hydrocarbon $C_{42}H_{46}$ (III) has already been described.[2] The evidence indicated that this hydrocarbon was not the ethane (IV) but its stable rearrangement product. This fact has now been definitely established by the synthesis of the ethane derivative. The following chart indicates the method used in this synthesis and summarizes the reactions of the two isomeric hydrocarbons which have been studied in the hope of furnishing evidence which will eventually make it possible to understand the rearrangement of this class of polyines.

[1] For references to earlier work, see Halley and Marvel, THIS JOURNAL, 54, 4450 (1932).

[2] Sweet and Marvel, *ibid.*, 54, 1184 (1932).



The new ethane (IV) was easily oxidized in the air and readily rearranged to the isomeric hydrocarbon, $C_{42}H_{46}$ (III). Chromium trioxide oxidized the ethane to benzophenone and the yield was 62%, which indicated that the two halves of this molecule really had the structure indicated. The ethane was readily cleaved with 40% sodium amalgam and yielded a sodium alkyl which could be converted to the acid (VII). The structure of this acid was established by oxidation with alkaline potassium permanganate to give principally benzophenone and a little benzoic acid. Chromium trioxide in acetic acid oxidized this acid to give primarily benzophenone (57%) but ring closures also occurred during the reaction because some o-benzoylbenzoic acid and traces of anthraquinone were isolated from the oxidation mixture.

The rearranged hydrocarbon, $C_{42}H_{46}$ (111), was not oxidized by oxygen. With potassium dichromate in acetic acid it was oxidized to a neutral compound $C_{36}H_{30}O_2$ (VIII). This product apparently resulted by the removal of two methyl and two ethyl groups and the addition of two atoms of oxygen. The neutral oxidation product absorbed four atoms of hydrogen when reduced catalytically with hydrogen in the presence of a platinum oxide catalyst.[3] These facts have been interpreted as meaning that the neutral compound is some type of diketone but no derivatives of the carbonyl group could be prepared. Oxidation of either the hydrocarbon, $C_{42}H_{46}$, or of the neutral oxygen compound $C_{36}H_{30}O_2$ by means of chromium trioxide in hot acetic acid gave benzoic acid and o-benzoylbenzoic acid. No benzophenone could be obtained from this oxidation reaction.

An unexpected reaction of the hydrocarbon $C_{42}H_{46}$ was its cleavage by 40% sodium amalgam to give a sodium alkyl which upon treatment with carbon dioxide yielded the same acid (VII) which had been obtained from the sodium alkyl prepared from either the methyl ether (V) or the true ethane (IV). However, the yields of acid from the rearranged hydrocarbon were never above 36%. This fact has been interpreted to mean that at least half of the molecule in the rearranged hydrocarbon must retain the carbon chain which was present in the original carbinol.

Further speculation on the structure of the rearranged hydrocarbon is useless until more evidence bearing on this rearrangement has been accumulated.

Experimental

Diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol [1,1-Diphenyl-4-methyl-4-ethylhexin-2-01-41 and the hydrocarbon $C_{42}H_{46}$ were prepared by the methods previously described.[2]

Methyl Diphenyl-(3-methyl-3-ethylpentinyl-1)-me Ether.—The carbinol was converted to the methyl ether by the general method which Moureu, Dufraisse and Blatt[4] used for diphenylphenylethinylcarbinol. To a solution of 14 g. of concentrated sulfuric acid in 140 cc. of absolute methyl alcohol cooled to 0° was added 14 g. of the carbinol over a period of about one minute. The mixture was stirred mechanically. A cloudiness developed in about three minutes and oily drops began to separate. Stirring was continued for about thirty minutes. The product was isolated by flooding with water and extracting with ether. The ether extract was washed with sodium bi-

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(3) Adams, Voorhees and Shriner, "Organic Syntheses," Collective Volume I, **1932,** p. **452.**

(4) Moureu, Dufraisse and Blatt, *Bull. soc. chim.*, [4] **35, 1412 (1924).**

carbonate solution, dried over anhydrous magnesium sulfate and distilled. The residual oil was purified by three distillations under reduced pressure. The yield was 12.5 g. (85% of the theoretical amount); b. p. 143–147° (0.32 mm.); n^{20}_{D} 1.5410; sp. gr.$^{20}_{20}$ 0.9892.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.21; H, 8.56. Found: C, 86.21, 86.15; H, 8.61, 8.58.

Diphenyl-(3-methyl-3-ethylpentinyl-1)-methyl-sodium.—To a solution of 9 g. of the above methyl ether in 250 cc. of anhydrous ether was added 15–20 cc. of 40% sodium amalgam. Air was excluded by flushing out the flask with dry nitrogen. The flask was tightly stoppered and shaken vigorously. A dark green color appeared at once and this changed to a deep red in about five minutes. Shaking was continued for about five hours. The sodium alkyl was not isolated but used in this solution.

Diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic Acid.—The sodium alkyl prepared from 1 g. of the methyl ether was treated with dry carbon dioxide and the organic acid was isolated in the usual fashion. After four recrystallizations from petroleum ether (b. p. 90–100°), 0.616 g. (59% of the theoretical amount) of the acid melting at 141–142° (Maquenne block) was obtained. In a capillary tube the acid softened at 140° and melted at 153–154°. The solution of the acid in carbon tetrachloride did not decolorize an appreciable amount of a solution of bromine in carbon tetrachloride. The acid did not decompose on heating to 170°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.45; H, 7.54; neutral equivalent, 320; mol. wt., 320. Found: C, 82.46; H, 7.60; neutral equivalent, 316, 319; mol. wt. (Rast), 282, 310.

Oxidation of Diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic Acid. **(a)** With Chromium Trioxide.—One gram of the acid was oxidized by adding it to a solution of 4 g. of chromium trioxide in 50 cc. of glacial acetic acid. The oxidation mixture warmed up to about 45° from the heat of the spontaneous reaction. The mixture was then boiled under a reflux condenser for about three hours. After cooling the mixture, it was poured into water and the water solution was extracted with ether. By extracting the ether with dilute sodium hydroxide and then acidifying the alkaline solution, a mixture of water-insoluble acids was obtained. This mixture was dried and then warmed on a boiling water-bath under a pressure of 25 mm. About 0.02 g. of benzoic acid, m. p. 118–120°, sublimed from the mixture. The material which did not sublime was recrystallized from carbon tetrachloride two or three times and then melted at 126–127°. The yield was about 0.02 g. This material was identified as o-benzoylbenzoic acid by a mixed melting point determination.

The ether solution remaining after the removal of the acidic portion with alkali was evaporated. On standing overnight a few yellow crystals separated from the oily residue. These crystals melted at 280° and were identified as anthraquinone.

The remaining oil was dissolved in about 10 cc. of alcohol and to the solution was added 3 cc. of 10% sodium hydroxide 0.5 g. of hydroxylamine hydrochloride and just enough water to cause the hydrochloride to dissolve. The resulting solution was refluxed for about twenty minutes and then allowed to stand at room temperature for two to three hours. The reaction mixture was poured into about four volumes of water, exactly neutralized with hydrochloric acid and cooled in an ice-bath. The yield of benzophenone oxime, m. p. 135–136, was 0.35 *g.* (57% of the theoretical amount). After crystallization from 50% alcohol the m. p. was 140–141° and when mixed with authentic benzophenone oxime the melting point was not changed.

(b) With Potassium Permanganate.—A mixture of 1 *g.* of the acid, 7 g. of potassium permanganate and 100 cc. of 1% potassium hydroxide solution was stirred until the spontaneous reaction ceased and then gently refluxed for about three hours. The mixture was acidified with sulfuric acid and filtered The precipitated manganese dioxide was thoroughly washed with ether and this ether was used to extract the aqueous filtrate. From this ether solution, 0.055 g. of benzoic acid m. p. 121–121.5° was isolated by extraction with alkali. The neutral material in the ether was treated with hydroxylamine as described above and 0.35 g. (57% of the theoretical amount) of benzophenone oxime, m. p. 139–140° was obtained.

Tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane [6,6,7,7-Tetraphenyl-3,10-dimethyl-3,10-diethyl-dodecadi-ine-4,8].—The cold solution of the sodium alkyl prepared from 2.5 g. of the methyl ether was decanted from the excess amalgam in an atmosphere of dry nitrogen. To the cold solution was added dropwise (about 20 cc.) a 10% solution of tetramethylethylene bromide in dry ether. The addition was stopped when no further change in the color of the solution was observed. The cold ether solution was filtered and the precipitate was washed thoroughly with ether. The filtrate and washings were evaporated under reduced pressure to about 20 cc. and 20 cc. of cold absolute alcohol (cooled to 0°) was added. The solution was finally cooled in a carbon dioxide–acetone bath for about thirty minutes and quickly filtered. The product was washed with ice-cold alcohol and ether and dried in a vacuum desiccator at 0° for about one hour and a half. The yield was 1.05 g. of white crystalline product, m. p. 140–142° (Maquenne block). By the capillary tube method a sample melted at 125–126° when placed in a bath previously heated to 120".

The ethane did not keep well and even at 0° began to decompose and rearrange in a short time. Analysis of a product which had stood long enough to be dry, always indicated that some oxidation had occurred. The compound was therefore characterized by its reactions.

Cleavage of the Ethane.—To a solution of 0.4 g. of the ethane in 30 cc. of anhydrous ether was added 5 cc. of 40% sodium amalgam. The flask was flushed out with nitrogen, securely stoppered and placed on a shaking machine. The solution quickly turned brown. The color changed to red in about four minutes. After about two hours, the sodium alkyl was treated with dry carbon dioxide and the reaction mixture was worked up to obtain diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic acid. After one crystallization from petroleum ether (b. p. 60–70") the yield of acid (m. p. 141–144°), was 0.16 g. (34% of the theoretical amount). Recrystallization gave a product melting at 153–154° (capillary tube method) which was shown by mixed melting point determination to be identical with the acid previously described.

The ethane in ether solution did not give a colored solution when treated with 1% sodium amalgam.

Oxidation of the Ethane. (a) With Oxygen.—One gram of the ethane was placed in 100 cc. of purified petroleum ether (b. p. 90–100") in a flask mounted on a shaker and connected to a gas buret filled with oxygen. The absorption of gas was very rapid and 84 cc. of oxygen (28°, 745 mm.) was absorbed within a minute. The quantity of oxygen for one mole to be absorbed by one mole of hydrocarbon was 43 cc. After permitting the mixture to shake overnight in an atmosphere of oxygen, the solvent was removed under reduced pressure at a temperature below 40°. The brown oil which remained was dissolved in ether. No acid could be isolated in sufficient quantity for identification by extracting this ether solution with aqueous sodium hydroxide. The ether solution was evaporated and the neutral oil which remained was treated with hydroxylamine as described above. White crystalline benzophenone oxime (0.06 g.), m. p. 138.5–139.5°, was obtained.

(b) With Chromium Oxide.—To a mixture of 3 g. of chromium trioxide and 40 cc. of glacial acetic acid at 20°, 0.4 g. of the ethane was added in portions. The oxidation mixture was stirred vigorously during the addition of the ethane, and held at about 20–25° for a day. It was then slowly warmed to 95°. After the reaction seemed complete, the mixture was cooled to about 50° and poured into 100 cc. of water. The water solution was extracted with ether. The ether solution was extracted with dilute sodium hydroxide solution but no water-insoluble acid was obtained by acidifying the alkaline extract. The ether solution was evaporated. The remaining oil was treated with hydroxylamine as already described and 0.18 g. (62% of the theoretical amount) of benzophenone oxime, m. p. 139.5–140.5°, was obtained.

Rearrangement of the Ethane.—A solution of 0.2 g. of the ethane in about 15 cc. of dry ether was slowly concentrated under reduced pressure. The residual material was washed once with absolute alcohol previously cooled to 0°. The crystals which remained weighed 0.1 g. and melted at 106–108.5°. After one recrystallization from absolute alcohol, pure rearranged hydrocarbon, $C_{42}H_{46}$, m. p. 106.5–108°, was obtained. This sample showed no depression in melting point when mixed with a sample of the hydrocarbon prepared by the reduction of the carbinol with titanium trichloride.

Oxidation of the Rearranged Hydrocarbon, $C_{42}H_{46}$. (a) With Potassium Dichromate in Acetic Acid.—The oxidation of the hydrocarbon $C_{42}H_{46}$, reported by Sweet and Marvel[2] was repeated. From 3 g. of the hydrocarbon, 0.94 g. of the neutral oxidation product, m. p. 137–138°, was obtained.

Anal. Calcd. for $C_{36}H_{30}O_2$: C, 87.41; H, 6.12; mol. wt. 494. Found: C, 87.01; H, 6.04; mol. wt. (Rast), 490.

In addition to this neutral oxidation product, about 0.1 g. of o-benzoylbenzoic acid, m. p. 126–127°, was obtained.

(b) With Chromium **Trioxide.**—A solution of 2 g. of the hydrocarbon, $C_{42}H_{46}$, in 60 cc. of glacial acetic acid was treated with 4 g. of chromium trioxide and the solution was boiled for ten hours. From this oxidation 0.1 g. of o-benzoylbenzoic acid, m. p. 126–127°, and 0.28 g. of the indifferent oxidation product, $C_{36}H_{30}O_2$, m. p. 137–138°, were obtained.

(c) Other Oxidation Experiments.—Oxonized oxygen was passed into a solution of the hydrocarbon in carbon tetrachloride. The only compound which could be identified among the oxidation products was benzoic acid. This was isolated in extremely small amounts. Perbenzoic acid apparently did not attack the hydrocarbon.

Cleavage of the Rearranged Hydrocarbon, $C_{42}H_{46}$.—A solution of 1 g. of the hydrocarbon in 40 cc. of dry ether was shaken in an inert atmosphere with 6 cc. of 40% sodium amalgam. The solution appeared red after about six minutes when the temperature was about 35°. After shaking the mixture for fifteen hours, dry carbon dioxide was introduced. From the reaction mixture, 0.42 g. (36% of the theoretical amount) of diphenyl-(3-methyl-3-ethylpentinyl-1-)-acetic acid, m. p. 141° (Maquenne block), was obtained.

Reactions of the Neutral Compound, $C_{36}H_{30}O_2$.—A solution of 0.5 g. of the compound $C_{36}H_{30}O_2$ in 15 cc. of glacial acetic acid was treated with 1 g. of chromium trioxide and refluxed for about six hours. From this oxidation mixture 0.036 g. of hydrated o-benzoylbenzoic acid, m. p. 88–92°, was obtained. After drying and recrystallizing this acid from carbon tetrachloride, the melting point was 126–127°.

Ozone oxidation of the neutral compound gave traces of benzoic acid. Perbenzoic acid and sodium hypobromite did not oxidize the neutral compound.

A solution of 1 g. of $C_{36}H_{30}O_2$ in 130 cc. of absolute alcohol was reduced with hydrogen under pressure in the presence of 0.05 g. of platinum oxide catalyst.[3] The absorption of hydrogen was complete in fifteen minutes. The catalyst was removed by filtration and the alcohol solution was concentrated to a small volume. On cooling, crystals separated. After recrystallization from alcohol the yield of product was 0.16 g. The melting point of the pure product was 226.5–228° (corr.).

Anal. Calcd. for $C_{36}H_{34}O_2$: C, 86.70; H, 6.68; mol. wt. 498. Found: C, 86.83, 86.92; H, 6.99, 7.02; mol. wt. 489.

Although the analytical evidence indicated that $C_{36}H_{30}O_2$ was a diketone, no derivatives of the carbonyl group were obtained. Furthermore, the reduction product did not give reactions of the hydroxyl group although four atoms of hydrogen were apparently added to the diketone.

Summary

1. The polyine, tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane has been prepared. It is oxidized by air, cleaved by 40% sodium amalgam, and rearranges spontaneously to give a more stable isomeric hydrocarbon, $C_{42}H_{46}$.
2. Some reactions of the rearranged hydrocarbon $C_{42}H_{46}$ have been studied in the hope of establishing its structure. Cleavage by sodium amalgam has furnished evidence that at least half of the molecule retains the original carbon skeleton.
3. The question of final structure of the isomeric hydrocarbon $C_{42}H_{46}$ and the exact nature of the rearrangement by which it is formed must be left open until further evidence can be obtained.

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The Oxidation of Citric Acid

BY ADRIAN C. KUYPER

Except for the questionable procedure of Nordbo and Schersten[1] the only method for the quantitative determination of minute amounts of citric acid is that of Thunberg[2] which is based on the speed of decolorization of methylene blue in the presence of citric acid and the specific citric acid dehydrogenase of cucumber seed. With certain modifications,[3] this method, although time-consuming, has proved satisfactory but, as with other biological methods, trustworthy results are obtainable only at the cost of continuous checking of the uniformity of reagents and procedure. For the study of the metabolism of citric acid a precise microchemical method is greatly needed and the oxidation of citric acid by permanganate, with manometric measurement of the carbon dioxide evolved, offered some promise.

By analogy with the permanganate oxidation of lactic acid by Avery and Hastings,[4] in which 1 mole of carbon dioxide is obtained from each mole of lactic acid, the production of 3 moles of carbon dioxide per mole of citric acid should be expected, especially since the commonly used quanti-

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(1) Nordbo and Schersten, *Skand. Arch. Physiol.*, *63*, 124–132 (1931).
(2) Thunberg, *Biochem. Z.*, 206, 109 (1929).
(3) Kuyper and Mattill, *Proc. Soc. Expt. Biol. Med.*, *28*, *863* (1931).
(4) Avery and Hastings, *J. Biol. Chem.*, *94*, 273 (1931).

tative methods for citric acid are based on the formation of acetone[5] or pentabromoacetone[6] by permanganate oxidation. It is specified in these methods that the solution must be kept boiling[5] or that the temperature may not rise above 60°[6] but even with this clue as to the possible influence of temperature it was surprising to find (Table I) that the oxidation of citric acid by 0.1 *N* and 0.2 *N* permanganate at room temperature in the Van Slyke constant volume apparatus gave not 3 moles but 4.64 moles of carbon dioxide per mole of citric acid, and with *N* permanganate 4.91 moles of carbon dioxide. As shown by Avery and Hastings with lactic acid, the smaller the concentration of citric acid, the more complete is the oxidation, until as many as five of the carbons appear as carbon dioxide. With very small amounts of citric acid the experimental error is, of course, magnified.

TABLE I

PERMANGANATE OXIDATION OF LACTIC AND CITRIC ACIDS IN VAN SLYKE MANOMETRIC APPARATUS

Acid used	Mml. per liter	Temp., °C.	$KMnO_4$, normal	Carbon dioxide, mml.	Mml CO_2 / mml acid (C → CO_2)
Lactic	0.652	25.3	0.1	0.643	0.985
Lactic	.590	23.2	.2	.592	1.004
Citric	.0944	25.0	.1	.438	4.64
Citric	.180	27.0	.2	.836	4.64
Citric	.0918	23.0	1.0	.454	4.94
Citric	.510	26.3	0.1	2.270	4.45
Citric	.255	26.4	.1	1.171	4.59
Citric	.1275	27.0	.1	0.609	4.78
Citric	.0637	27.0	.1	.303	4.75
Citric	.0318	27.3	.1	.154	4.85
Citric	.0159	27.2	.1	.0655	4.12
Citric	.00795	27.2	.1	.0406	5.10

This paradox, more complete oxidation at room temperatures than at higher temperature, was demonstrated in another may by titration of citric acid with permanganate in sulfuric acid at various temperatures within the range of 20–100°. The data in Table II show that between 60 and 70° the nature of the oxidation reaction changes. Below this point 1 mml. of citric acid consumed 3 mml. of permanganate oxygen, with a small temperature gradient. Above that point the permanganate oxygen consumption per mml. of citric acid declined, until at boiling temperature the amount of permanganate used per mml. of citric acid was about half that used at 57–63°. Also acetone appeared above that point (qualitative colorimetric estimation), but none below it. The less vigorous oxidation in acetic acid solution (Table 11) revealed the same behavior; at boiling temperature some citrate was still oxidized beyond the acetone

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(5) Kogan, Z. *anal. Chem.*, *80, 112* (1930).

(6) Hartmann and Hillig, *J. Assn. Off. Agric. Chemists,* **10, 264 (1927)**.

TABLE II

PERMANGANATE OXIDATION OF CITRIC ACID AT DIFFERENT TEMPERATURES

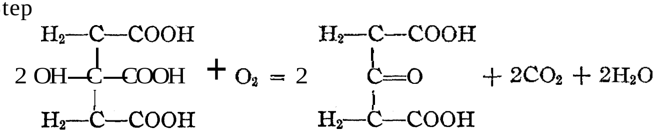
Acid oxidized	Mml. per liter	Acid	Temp., °C.	$KMnO_4$, cc.	Oxygen, mml.	Mml oxygen / Mml. acid	Acetone
Citric	2.285	H_2SO_4	15–20	61.50	6.96	3.05	0
Citric	2.285	H_2SO_4	27–30	63.00	7.13	3.12	0
Citric	2.285	H_2SO_4	37–40	63.25	7.18	3.14	0
Citric	2.285	H_2SO_4	57–63	64.20	7.28	3.19	0
Citric	2.285	H_2SO_4	77–83	51.00	5.78	2.53	2+
Citric	2.285	H_2SO_4	87–93	46.80	5.33	2.33	5+
Citric	2.285	H_2SO_4	93–103	32.60	3.70	1.62	5+
Citric	0.815	Acetic	60–65	7.10	0.814	1.00	
Citric	1.63	Acetic	Boiling	8.10	.930	0.571	
Acetone dicarbonic	0.699	H_2SO_4	26	16.70	1.795	2.57	0
Acetone dicarbonic	699	H_2SO_4	65	14.30	1.632	2.34	Trace
Acetone dicarbonic	.699	H_2SO_4	Boiling	0.00	0.000	0.00	5+

stage (0.571 instead of the theoretical 0.500) which explains why Kogan's method recovers only 89% of the theoretical amount of acetone.

An insight into the mechanism of the two different reactions above and below 60° was provided by the behavior of an intermediary product,[7] acetone dicarbonic acid (Table II), which paralleled that of citric acid, except that at boiling temperature acetone dicarbonic acid consumed no permanganate oxygen and decomposed spontaneously into carbon dioxide and acetone.

The following equations have been formulated to explain the divergent course of citric acid oxidation as influenced by temperature.

First Step

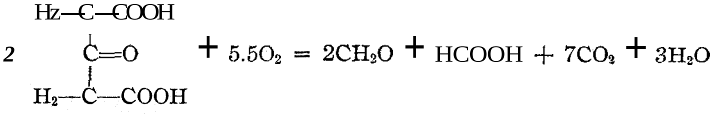


$$2\,\begin{array}{c}H_2\text{—C—COOH}\\ |\\ \text{OH—C—COOH}\\ |\\ H_2\text{—C—COOH}\end{array} + O_2 = 2\,\begin{array}{c}H_2\text{—C—COOH}\\ |\\ \text{C=O}\\ |\\ H_2\text{—C—COOH}\end{array} + 2CO_2 + 2H_2O$$

Citric acid Acetone dicarbonic acid

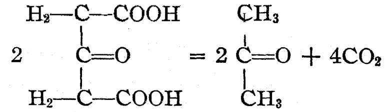
Second Step

At low temperature



$$2\,\begin{array}{c}H_2\text{—C—COOH}\\ |\\ \text{C=O}\\ |\\ H_2\text{—C—COOH}\end{array} + 5.5O_2 = 2CH_2O + HCOOH + 7CO_2 + 3H_2O$$

At high temperature



$$2\,\begin{array}{c}H_2\text{—C—COOH}\\ |\\ \text{C=O}\\ |\\ H_2\text{—C—COOH}\end{array} = 2\,\begin{array}{c}CH_3\\ |\\ \text{C=O}\\ |\\ CH_3\end{array} + 4CO_2$$

The first stage in the oxidation at any temperature is the formation of acetone dicarbonic acid. Additional evidence for this statement is that

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(7) Wohlk, *Z. anal. Chem.*, **41**, 77 (1902).

this acid and citric acid are the only substances of this general structure which quantitatively yield a pentabromoacetone derivative when oxidized in the presence of potassium bromide.[8] The nature of the second step depends on the relationship between the temperature and the speed of oxidation. At high temperature acetone dicarbonic acid is decomposed to acetone but if the oxidizing potential is high some of it may be oxidized. The oxidative reaction is accelerated by the use of sulfuric instead of acetic acid, or by increasing the strength of the permanganate solution. Indeed, an almost purely oxidative reaction can he secured even at high temperatures by very rapid addition of permanganate.

The reaction at room temperatures is equally variable and because of its immediate relation to the original purpose of the work it was studied in greater detail. Apparently the only products are formaldehyde, formic acid and carbon dioxide in variable amounts. Citric acid was titrated with acid permanganate in a closed flask, such that the carbon dioxide could be aerated from the solution and weighed, The formic acid remaining in the reaction mixture was determined by the weight of mercurous chloride produced by the reducing action on mercuric chloride.[9] No means was found for making simultaneous determinations of formaldehyde and carbon dioxide, and since separate determinations in different runs have no value because of the variability of the reaction, the amount of formaldehyde formed was calculated as representing the carbon which entered the reaction less that found as formic acid and carbon dioxide at its completion, a procedure which was later justified. From the observed and calculated data the oxygen entering the reaction in citrate and permanganate was compared with that found in the oxidation products. Table III presents the results of a series of titrations at room temperature in which the rate of addition of permanganate was gradually reduced. With rapid addition of permanganate the amount of oxygen found in the reaction products was equal (within 0.5%) to that present in the original citrate plus that derived from the permanganate used. As the speed of permanganate addition was reduced (Experiments 2 to 8) the reaction products contained increasingly more oxygen (finally 28% more) than is known to have entered the reaction as citrate and permanganate. The formation of less highly oxidized products is improbable; neither acetone nor other partial oxidation products could be detected and any calculation on the basis of their formation still fails to account for the additional oxygen present. When nitrogen was used for aeration (Experiments 9, 10), whether permanganate was added fast or slowly, no excess oxygen was recovered; on the other hand, when the solution was aerated very slowly with oxygen (Experiment 11), the products contained almost 36% excess

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[8] Amberg and McClure, *Am J. Physiol.*, 44, 453 (1917).

[9] Autenrieth and Warren, "Detection of Poisons," P. Blakiston's Son and *Co.*, Philadelphia. 1928, 6th ed., p. 98.

TABLE III

OXYGEN BALANCE IN CITRIC ACID OXIDATION AT ROOM TEMPERATURE

	Oxygen entering the reaction			Oxygen in the end products of the reaction						Remarks	
Expt.	Citrate[a] mml.	$KMnO_4$, mml.	Total, mml.	Formic acid, mml.	Carbon dioxide, mml.	Formaldehyde[b] mml.	Water[c] mml.	Total	Oxygen "recovery," %	Aerated with	$KMnO_4$ added
1	3.500	3.626	7.127	0.978	4.674	0.173	1.337	7.163	100.49	Air	Fast
2	3.500	3.545	7.044	1.016	4.706	.138	1.332	7.215	102 44	Air	
3	3 500	3.336	6.835	0.607	4.788	.302	1.394	7.094	103.78	Air	
4	3.500	3.440	6.942	.721	4.822	.229	1.411	7.182	103.47	Air	
5	3.500	3.334	6.833	.627	4.939	.216	1.470	7.252	106.12	Air	to
6	3.500	3.108	6608	.589	4.985	.213	1.492	7.280	110.15	Air	
7	3.500	2.405	5.905	.265	4.808	.462	1.404	6.940	117.55	Air	
8	3.500	2 467	5 967	.266	5.512	.110	1.757	7.645	128.13	Air	Slowly
9	3.500	3 628	7.129	.730	4.653	.308	1.326	7.019	98.46	Nitrogen	Slowly
10	3.500	3.775	7.276	1.116	4.665	.160	1.282	7.124	97.93	Nitrogen	Fast
11	3.500	2.170	5.670	0.206	5.590	.102	1.795	7.694	135.70	Oxygen	Slowly

[a] From 0.9 to 1.7 mml. of citrate was used in these experiments. The results were all recalculated to 1 mml. of citric acid which contains 3.5 mml. of oxygen.

[b] The oxygen present in formaldehyde was calculated as equal to one-half the difference between the carbon entering the reaction and that recovered as formic acid and carbon dioxide, all expressed as millimoles

[c] This value was obtained by considering the oxidation of citric acid as occurring in three separate reactions involving the formation of the determined amounts of formic acid, carbon dioxide and formaldehyde, respectively. The water taking part in each reaction was then calculated, the values were summated, and the oxygen equivalents obtained.

oxygen. Molecular oxygen therefore enters the reaction and in part supplants permanganate. An almost 100% recovery in the reactions aerated with nitrogen confirms the original assumption that permanganate oxidation of citric acid at room temperature produces only carbon dioxide, formaldehyde, formic acid and water. The small amount of oxygen unaccounted for in the nitrogen aerations may have been lost in volatilized formic acid.

The distribution of oxygen in the various end-products requires comment. The total amount of formaldehyde and formic acid produced per mole of citrate oxidized decreases with increasing participation of molecular oxygen (from considerably above 1 mole to less than half a mole); the amounts of carbon dioxide and water produced increase with increasing participation of molecular oxygen. Furthermore, when molecular oxygen is most instrumental in oxidation (Experiment 11), it enters the reaction in the ratio of two moles for each mole of citrate oxidized. This amount is just sufficient to oxidize one mole of acetone dicarbonic acid to three moles of carbon dioxide, one of water and two of formaldehyde. Three of its carbon atoms are already oxidized to or beyond the formaldehyde stage; the remaining two are probably oxidized by the same path. Acetone dicarbonic acid, perhaps in an active state, is therefore the most likely intermediate substance to react with molecular oxygen; permanganate is thereby released for the more complete oxidation of formaldehyde and formic acid to carbon dioxide.

These observations explain some of the difficulties encountered in the quantitative estimation of citric acid by permanganate oxidation. Duplicate results are obtainable only under exactly similar conditions, In Kogan's method slight changes in temperature, acidity and rate of addition of permanganate influence the amount of acetone produced. In the oxidation to pentabromoacetone an empirical conversion factor of 1.05 indicates that some citrate is oxidized beyond this stage. Oxidation by ceric sulfate[10] apparently also requires careful control of acidity, volumes and concentrations of the reacting substances, and according to its sponsors "the conversion factor indicates very extensive oxidation of acetone." By means of the conversion factors given in Table I citric acid in pure solutions can also be determined satisfactorily by the Van Slyke constant volume apparatus, provided standardized conditions are maintained.

The association of molecular oxygen with permanganate in the *in vitro* oxidation of citric acid at temperatures below 60° is interesting in the light of the rapid oxidation of this substance in the animal body. Its failure to produce acetone at body temperature *in vitro* agrees with the observation[11] that it is an antiketogenic substance.

The author wishes to thank Professor H. A. Mattill for his interest and assistance.

Summary

The acid permanganate oxidation of citric acid is more complete at room temperatures than at high temperatures. Acetone dicarbonic acid is the first intermediary product. At temperatures below 60°, depending on the concentration of permanganate and the rate of its addition, this intermediary product is oxidized to formaldehyde, formic acid and carbon dioxide; molecular oxygen takes part in this oxidation and no acetone is formed. The higher the temperature above 60° the more acetone dicarbonic acid is decomposed into acetone before it can be oxidized.

By means of proper conversion factors small amounts of citric acid in pure solution may be determined by oxidation with permanganate in the Van Slyke constant volume apparatus.

IOWA CITY, IOWA RECEIVED NOVEMBER 21,1932
PUBLISHED APRIL 6, 1933

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(10) Willard and Young, THIS JOURNAL, 52, 132 (1930).
(11) Greenwald, *J. Biol. Chem.*, 18, 115 (1914).

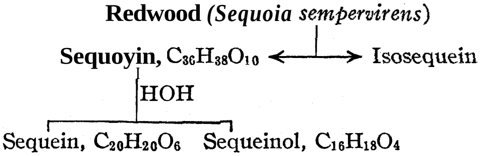
[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE

The Crystalline Coloring Compounds in Redwood Extract[2]

BY E. C. SHERRARD AND E. F. KURTH

The heartwood of freshly cut green redwood is usually of a straw color. Soon after the surface is exposed to the atmosphere a red to brown discoloration develops. This paper describes the isolation and several properties of two crystalline coloring substances which, together with certain of their derivatives, may be responsible for the red and brown colors in seasoned redwood. In naming these compounds an attempt was made to conform as nearly as possible to the nomenclature used by Perkin and Everest[3] on coloring matter of similar nature.

The compounds and the relationship of a few derivatives are



One of the compounds, *sequoyin,* crystallizes when pure in white or pink flakes, melting at 214° (uncorr.). The other substance, *isosequein,* has been obtained from only two redwood specimens, but its presence is apparent in most redwood liquors. It crystallizes in clusters of red needles, melting sharply at 188°. Its isolation is made difficult by the presence of a relatively large amount of gums, tannins, phlobaphenes and other soluble material in redwood. All treatments that remove these impurities also remove the color compound.

Sequoyin appears to be best obtained by lixiviating green or seasoned redwood in the form of sawdust or chips with distilled water at room temperature. The product is concentrated to a thick sirup by distillation under reduced pressure. The distillate thus obtained is colorless and apparently is free from any appreciable quantity of volatile material. The black residue in the distilling flask is extracted several times with ether. Upon evaporation of the ether, crystallization takes place, usually within a few days. The ether extract from most samples of sawdust crystallized within twenty-four hours, while other extracts from a different source of wood failed to crystallize satisfactorily when given several weeks. The best yield of crystals is obtained from sound wood that has been recently felled. Acetic acid is invariably a component of the ether extract

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(1) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

(2) This is part of a paper presented at the seventy-ninth annual meeting of the American Chemical Society at Atlanta, Ga , April 7–11, 1930.

(3) Perkin and Everest, "The Natural Organic Colouring Matters," Longmans, Green & Co.. London, 1918.

After crystallization of the concentrated ether extract has occurred, the crystals are purified by dissolving them in hot alcohol and precipitating once or twice with benzene and finally with water. The crystals thus obtained are thin, glistening flakes, odorless and tasteless. They are slightly soluble in cold water, more freely in hot water, slightly soluble in ether, soluble in glacial acetic acid and very soluble in alcohol. They dissolve readily in dilute alkalies, giving a bright red which gradually changes at the surface to a brown, forming at the same time a brown amorphous precipitate. This brown material exists in considerable quantity in redwood liquors. In cold concentrated sulfuric acid, the crystals dissolve with a deep red color. They burn with a luminous flame, giving an odor of a phenol and leave no ash.

Anal. Found: C, 68.7, 68.4, 68.4; H, 6.13, 6.07, 6.17; nitrogen, sulfur and halogen are absent.

Molecular weight determinations with absolute alcohol by the ebullioscopic method, with glacial acetic acid by the cryoscopic method, and with camphor by the method of Rast,[4] did not give consistent values.

With lead acetate and with stannous chloride, sequoyin gives a white colloidal precipitate that is not stable in the presence of alkali; with ferric chloride a permanent green is produced. It reduces Tollens' ammoniacal silver nitrate reagent very readily but gives no precipitate of cuprous oxide with Fehling's solution. Methoxyl (OCH_3), carboxyl ($COOH$) and carbonyl (CO) groups apparently are absent. Acetylation with acetic anhydride at 100° yields white microscopic crystals melting at 104 to 106°.

The percentage acetyl (CH_3CO) of these crystals, as determined by the method of Perkin,[5] equals 35.8 to 35.3%.

The properties just described fail to correspond with those of any substance previously described in the literature. The empirical formula suggested for sequoyin is $C_{36}H_{38}O_{10}$. More information in favor of this formula will appear later in this report. Calcd. for $C_{36}H_{38}O_{10}$: C, 68.6; H, 6.08; CH_3CO for octaacetate, 35.7.

By dry distillation or fusion with potassium hydroxide, a dark brown oil having a decided phenolic odor is obtained. It has not been characterized, as the amount obtained was very small, and appears to be a mixture of two or more phenolic substances. Fusion with glycerin at 200 to 210° for three-quarters of an hour gives two compounds melting at 185 and 216°, respectively.

Preparation of **Sequein** and **Sequeinol.**—Upon heating sequoyin with 5% sulfuric acid for several hours, two crystalline compounds may be obtained. They appear together or separately upon cooling the solution. They are separated from one another by fractional crystallization; sequein, which is the more soluble in alcohol, crystallizes in long slender white needles that melt sharply at 190" (uncorr.) when pure. The other, sequeinol, crystallizes from hot dilute alcohol in short needles that melt with some decomposition at 242° (uncorr.).

Sequein has properties similar to the parent substance. It has been obtained in yields up to 50.0%. It crystallizes from slightly acid solutions with water of crystallization, which it loses at 100 to 105°. The crystals are white, but after drying in a desiccator they become brown externally. When white they are tasteless, but after becoming brown they are bitter. Heated at temperatures above its melting point it decomposes and leaves a bulky carbonaceous residue. It is only slightly soluble in cold water, more so in hot water and is dissolved with facility by alcohol. Sodium bicarbonate solution dissolves it incompletely. Sequein could be used as an indicator, its tincture being very sensitive to free alkalies and alkaline salts, with which it gives a bright red, while with acids it is yellow. It exhibits phenolic properties, adds bromine,

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(4) Rast, Ber.. SSB, 1051–1054 (1922).

(5) Perkin, *J. Chem. Soc.*, 87, 107 (1905).

and an alcoholic solution produces a transient green with ferric chloride. Basic lead acetate yields a violet precipitate, which gradually darkens on exposure to the air. Neutral lead acetate produces a slight reddish precipitate, the filtrate of which is a bright red. Stannous chloride gives a permanent rose-colored precipitate. An ammoniacal solution becomes a bright cherry red, ultimately changing to a brown. Upon the addition of acetic acid to this brown solution a brown precipitate is deposited. This precipitate fuses at temperatures over 250° and burns completely without the formation of ash. It gives a deeper shade of red with alkalies than the original compound. With potassium permanganate, sequein is oxidized to a brown humus-like substance that is devoid of any color-producing properties, while with nitric acid, oxalic acid (m. p. 99°) has been obtained. Sequein gives no precipitate with Fehling's solution, nor is it affected by phenylhydrazine. With hydrogen chloride in a dry ethereal solution, it forms a red oil from which the crystals (m. p. 190°) are again obtained upon bringing in contact with water. Wool mordanted with potassium bichromate is dyed a reddish-brown.

Anal. Found: C, 67.40, 67.36; H, 5.63, 5.59.

Molecular weight determinations by the method of Rast using camphor as a solvent gave 356 and 358; by the ebullioscopic method using absolute alcohol as a solvent the values 345 and 336 were obtained.

The above analyses, therefore, correspond to a compound of the empirical formula $C_{20}H_{20}O_6$.

Calculated for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66; molecular weight, 356.16

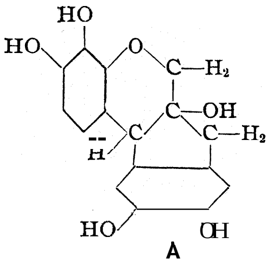
Preparation of Sequein Hexaacetate.—Sequein is acetylated by boiling with acetic anhydride with or without the aid of a catalyst, such as sulfuric acid, and also with acetic anhydride and pyridine at room temperatures. Upon adding water to the cooled reaction mixture, the acetylated derivative separates out. After recrystallizing from hot alcohol it may melt at 124 or at 114°. The lower-melting derivative is the one most commonly obtained. The difference in melting points is undoubtedly due to the formation of two isomers.

Analyses on the acetylated derivative, m. p. 114": Found: C, 62.62, 62.71; H 5.43, 5.41; acetyl (CH_3CO), 42.1, 42.2.

Molecular weight, average of several determinations, gave 607. These values calculated for a hexaacetate compound. Calcd. for $C_{20}H_{14}O_6 \cdot 6(CH_3CO)$: C, 63.13; H, 5.32; CH_3CO, 42.4; molecular weight, 608.25.

Attempts to characterize the products of degradation of sequein were not successful in that only a small amount of the pure compound was available. Fusion with potassium hydroxide, or dry distillation with diminished pressure, yields a brown oil having a very pronounced phenolic odor. During dry distillation orange-colored crystals may be seen momentarily in the receiving flask before dissolving in the distillate.

The residue from the hydrolysis of the acetylated product does not again give the original compound. Upon extracting the acid residue with ether, a red film is formed when the solvent is evaporated. This material dissolves readily in dilute sodium hydroxide with a purple color and is precipitated as a brown oil upon the addition of an acid. All attempts to induce it to crystallize have failed. Upon exposure to the air it gradually darkens to a black granular mass.



A

Of the naturally occurring coloring principles the properties of sequein approach those of the dihydropyran group, of which hematoxylin and brasilin are the most important representatives. Brasilin is obtained from *Caesalpinia braziliensis,* while hematoxylin is derived from *Hematoxylon campeachianum*. The constitutional formula of hematoxylin accepted by W. H. Perkin and his co-workers after a series of extensive researches is shown as (A). On oxidation, hematoxylin gives rise to the actual dyestuff hematein, which dissolves in alkalies with a deep red color that is destroyed by excessive oxidation. Sequein has a larger molecule than hematoxylin, by reason of one or more side chains.

On the Properties of Sequeinol.—Sequeinol is soluble in alcohol and is insoluble in cold water, sodium carbonate solutions or carbon tetrachloride. With dilute alkalies it dissolves readily without color and is precipitated from alkaline solutions as microscopic needles with carbon dioxide or with dilute acids. It contains, therefore, no carboxyl group, but has phenolic properties. A clear emerald color is obtained with ferric chloride in 95% alcohol. Fused with finely ground potassium hydroxide at 220° for twenty minutes, it retains its original melting point, 242°.

Anal. Found: C, 69.97, 69.97; H, 6.55, 6.53.

Molecular weight by the ebullioscopic method using absolute alcohol as a solvent gave 280 and 288.

These values correspond for a compound with the empirical formula $C_{16}H_{18}O_4$: Calcd. for $C_{16}H_{18}O_4$: C, 70.03; H, 6.61; molecular weight, 274.14.

Preparation of Sequeinol Tetraacetate.—Heating with acetic anhydride in a water-bath with or without sodium acetate gave a product which crystallized from hot alcohol in short needles melting at 176 to 177° (uncorr.). The percentage acetyl of these crystals when determined by the method of Perkin was 38.51. Molecular weight determinations gave 446 and 466. Calcd. for $C_{16}H_{14}O_4 \cdot 4(CH_3CO)$: CH_3CO, 38.68; molecular weight, 442.2.

Results indicate that there are four hydroxyl groups in sequeinol. No compound with like properties has been found in the literature.

On dry distillation under reduced pressure an amber-colored oil is obtained as a distillate. It is insoluble in water, benzene and carbon tetrachloride, but is dissolved with facility by alcohol or ether. An aqueous suspension with ferric chloride gives a transient yellow-green color. With the addition of dilute sodium bicarbonate to this ferric chloride solution a red color is formed which indicates the presence of catechol.[6]

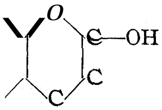
From the residue remaining from the acetyl determinations of sequeinol, small hard brown crystals are obtained. They melt at 218°, bum with a luminous flame, and leave no ash. They are insoluble in water, soluble in hot alcohol, give no color with ferric chloride and are precipitated instantly from alkaline solutions with acids.

On the Constitution of Sequoyin.—The acid filtrate from the hydrolysis of sequoyin reveals nothing of importance. It contains no reducing material, which demonstrates the absence of sugars in sequoyin.

Sequeinol apparently is not a decomposition product of sequein. Further treatment of sequein with sulfuric acid under the conditions for the breaking up of sequoyin gave no additional sequeinol. A formula of the pyran type for sequein provides for a half acetal linkage with sequeinol in sequoyin. A labile half acetal linkage is the most logical to explain the splitting of the sequoyin molecule with a dilute mineral acid to form two compounds, both of which have no free carboxyl group.

(6) Allen, "Commercial Organic Analysis," 5th ed., Blakiston, Philadelphia, 1925, p. 338.

Sequein is, therefore, concluded to have a hydroxyl group on the carbon atom adjoining the oxygen in the pyran ring. Upon acetylating such a compound, the ring structure is very likely to be broken. This explains the formation of sequein hexaacetate, and also why sequein is not recovered again after the hydrolysis of sequein hexaacetate.



Sequoyin having the half acetal structure just mentioned should, therefore, have two of its ten oxygen atoms unaffected by acetylation. This is confirmed by experimental evidence in that the octaacetate derivative is obtained upon acetylation.

The summation of sequein and sequeinol less one H_2O taken up on hydrolysis is equivalent to the formula $C_{36}H_{36}O_9$. Our analysis of sequoyin demonstrates that it possesses the formula $C_{36}H_{38}O_{10}$. One molecule of water must, therefore, be lost during the process of hydrolysis.

On the Properties of **Isosequein.**—This compound was obtained from only two redwood specimens in the green condition. The amount available for experimental investigation was small. After repeated crystallizations from hot alcohol it was finally obtained in clusters of red needles, which melt sharply at 188°. A dilute solution gives a violet color gradually darkening with alkalies, which is of similar intensity and sensitivity to that produced when proportionately dilute unpurified redwood extracts are treated with alkali. In acid solutions it is yellow. It possesses phenolic properties, producing a dark green with ferric chloride.

Molecular weight determinations by the method of Rast gave 348 and 353. Structurally it is believed to be related to sequein.

Summary

Two crystalline red color-producing compounds, sequoyin and isosequein, have been isolated from the heartwood of redwood. These two compounds, together with their decomposition products, are believed to be largely responsible for the color changes in redwood. Through hydrolysis with dilute acids sequein and sequeinol have been obtained from sequoyin. The compounds do not appear to have been described in the literature previously.

MADISON. WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CXXXII.
A New Synthesis of Thymine

BY WERNER BERGMANN[1] AND TREAT B. JOHNSON

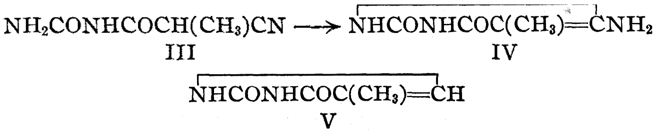
When in 1900 Wilhelm Traube[2] made his important contributions to our knowledge of pyrimidine chemistry, he was particularly interested in developing a new technique for the synthesis of purines of the uric acid type comparable to the classical methods of preparation previously described by Emil Fischer.[3] The compound which served as the starting point of his researches was cyanacetic acid. He found that this reagent combined smoothly with urea, thiourea and guanidine, giving acyclic ureides which easily undergo cyclic condensations, giving pyrimidine combinations that are easily transformed into purines. Traube's method of purine synthesis is limited to the use of cyanacetic acid or its ester and is applicable, therefore, only to oxypyrimidines, which are unsubstituted in position 5 of the pyrimidine ring. Presumably for this reason the action of the homologs of cyanacetic acid on urea, thiourea and guanidine, and the rearrangement of their respective condensation products have thus far been neglected. The development of a program of work in fields of heterocyclic chemistry calling for the application of new methods of pyrimidine syntheses is now leading to a study in this Laboratory of cyclic ureides derived from substituted cyanacetic acids of types I and II.

$$NCCHXCOOH \qquad NCCX_2COOH$$

I II

The use of a substituted cyanacetic acid of type I for the synthesis of thymine is described below.

As the rearrangement of cyanacetyl-urea leads to 4-aminouracil, that of methyl cyanacetyl-urea III should be productive of the corresponding amino derivative of thymine IV. Moreover, if as Rupe[4] found, cyanacetyl-urea is transformed by catalytic hydrogenation in the presence of platinum into uracil, then methyl cyanacetyl-urea III should under the same conditions be transformed into thymine V. Since thymine is not easily obtainable in quantity and any improvement in present methods of synthesis, therefore, is desirable, it seemed worth while to study these new reactions.



$$NH_2CONHCOCH(CH_3)CN \longrightarrow NHCONHCOC(CH_3){=}CNH_2$$

III IV

$$NHCONHCOC(CH_3){=}CH$$

V

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(1) Sterling Professorship of Chemistry Research Assistant.

(2) Traube, Ber., 33, 1374 (1900).

(3) Fischer, ibid., 20, 2251 (1897).

(4) Rupe, Helv. Chim. Acta., 8, 850 (1925).

Methyl cyanacetic acid, which can be prepared very easily according to the method of Hessler,[5] condenses smoothly with urea in the presence of acetic anhydride, forming the ureide III. We now find that this compound, when reduced catalytically, is transformed with evolution of ammonia into thymine as represented by the formulas above. The thymine prepared by this new method is obtainable in good yield, and free from sulfur and the pyrimidine uracil. It did not respond to the Wheeler–Johnson[6] color test for uracil and cytosine. There is no doubt that this technique when developed will serve for the preparation of many other uracil derivatives substituted in position 5 of the pyrimidine ring. Many of the combinations desired for our work cannot be prepared successfully through the usual methods calling for application of a Claisen ketone ester condensation with ethyl formate, followed by condensation with thiourea or 2 pseudo-thiourea to give a pyrimidine.

When treated with alkali methyl cyanacetyl-urea III undergoes a molecular rearrangement with cyclization to a pyrimidine ring forming 4-aminothymine or 2,6-dioxy-4-amino-5-methylpyrimidine IV, in the same way as cyanacetyl-urea is transformed into 4-amino uracil or 2,6-dioxy-4-aminopyrimidine.[7]

Experimental Part

Methyl Cyanacetyl-urea, 111.—One mole of methyl cyanacetic acid[6] and 1.1 mole of urea are heated with 1.25 moles of distilled acetic anhydride on a steam-bath. After twenty minutes' heating crystals begin to separate which increase in quantity very rapidly as the heating is continued until the liquid assumes a solid condition, when the reaction is complete. This ureide is purified by crystallization from hot water, in which it is very soluble. On cooling, it deposits in the form of plates melting at 192°. The crystals contained water of crystallization. For analysis the compound was dried at 100° in a vacuum.

Anal. (Micro.) 3.879 mg. gave 6.06 mg. of CO_2, 1.692 mg. H_2O. 2.933 mg gave 0.759 cc. of N_2 at 22° and 746 mm. Calcd. for $C_5H_7O_2N_3$: C, 42.55; H, 4.96; N, 29.79. Found: C, 42.62; H, 4.88; N, 29.40.

Thymine V.—Methyl cyanacetyl-urea is dissolved in about thirty times its weight of hot water and the solution agitated in an atmosphere of hydrogen at 70° using platinum black (Willstatter) as the catalytic agent. When one-half the theoretical quantity of hydrogen has been absorbed, heating is discontinued and the agitation continued until one mole of hydrogen has been absorbed The catalyst is then separated by filtration and the solution acidified with acetic acid to neutralize the ammonia liberated by hydrolysis. This base forms a salt with thymine, holding the latter in solution The solution is finally concentrated and cooled when thymine separates. After one recrystallization from boiling water it showed a melting point of 318–320°. The thymine obtained by this procedure showed all the typical thymine reactions and was free from uracil.

2,6-Dioxy-4-amino-5-methylpyrimidine (4-Aminothymine) **IV.**—Methyl cyanacetyl-urea III was dissolved in three times its weight of 20% aqueous sodium hydroxide solution and the mixture allowed to stand for half an hour. On acidifying with

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(5) Hessler, THIS JOURNAL, 35, 980 (1913).

(6) Wheeler and Johnson, *J. Biol. Chem.*, 3, 183 (1907).

(7) Traube, Ber., 41, 532 (1908).

acetic acid the 4-aminothymine separated in needles. This pyrimidine was purified by recrystallization from boiling water and melted at 355°. The rearrangement of the acylurea III into 4-aminothymine IV can also be effected by heating in aqueous solution with magnesium oxide. For analysis the compound was dried at 100° in a vacuum.

Anal. Calcd. for $C_5H_7O_2N_3$: N, 29.79. Found: N, 29.56.

Summary

1. Methyl cyanacetyl-urea can be rearranged to 2,6-dioxy-4-amino-5-methylpyrimidine by the action of alkali.
2. Methyl cyanacetyl-urea, when reduced catalytically in the presence of platinum is converted smoothly into thymine.

NEW HAVEN, CONNECTICUT

RECEIVED FEBRUARY 4, 1933
PUBLISHED APRIL 6, 1933

Notes

Preparation of Triethylsilicon Halides

BY E. A. FLOOD

It is commonly supposed that triethylsilicon halides cannot be prepared, readily, from di-triethylsilicon oxide. Nevertheless it has been found that triethylsilicon bromide, chloride and fluoride can be obtained very easily from the oxide by treating a mixture of concentrated sulfuric acid and di-triethylsilicon oxide with the corresponding sodium or ammonium halide. The mixture is allowed to stand for some hours and the product extracted with petroleum ether. The triethylsilicon halide is separated from the solvent by distillation. The yields are practically quantitative.

Triethylsilicon fluoride, prepared in this way, is a colorless mobile liquid having a very faint "camphor-like" odor. It boils at 110° (uncorr.) under atmospheric pressure. It is much more stable toward hydrolysis than is the corresponding bromide and may be distilled in air without appreciable decomposition.

Analyzed for fluorine by a modified Starck method, calcd. for $(C_2H_5)_3SiF$: F, 14.15. Found: F, 14.31, 14.63, mean 14.48.

It was shown to be a single substance as follows. About ten grams was allowed to distil under its own vapor pressure at room temperature into a receiver (volume 302 cc.) cooled to −33°. The vapor density of the first two or three drops of distillate collected was determined, as well as the vapor density of the last two or three drops of residual liquid remaining in the original container. The vapor densities of the two extreme fractions agreed within the experimental error and gave a value for the molecular weight in close agreement with that required by the formula $(C_2H_5)_3SiF$. The data follow: mol. wt. (vapor density). First fraction. Subs., 0.0534, 0.0501: vol., 302.0; pressure, mm., 24.7, 22.9; *t*, 27.7°, 28.0°.

Mol. wt. 134.3, 136.1, mean, 135.2. Last fraction. Subs., 0.0383, 0.0506; vol., 302.0; pressure, mm., 17.7, 22.9; *t*, 28.1, 28.5; mol. wt. 134.6, 137.6, mean, 136.2. Calcd. for $(C_2H_5)_3SiF$: mol. wt., 134.2.

CHEMISTRY DEPARTMENT
BROWN UNIVERSITY
PROVIDENCE, R. I.

RECEIVED JANUARY 5, 1933
PUBLISHED APRIL 6, 1933

A Hydrate of 1,3,5-Xylenoxyacetic Acid

BY ALAN R. ALBRIGHT

In a study of phenolic fractions obtained from coal tar, we have found it desirable to prepare derivatives of certain pure phenols for purposes of comparison. One of the derivatives which we prepared was the oxyacetic acid formed by interaction of symmetrical xylenol and chloroacetic acid in the presence of sodium hydroxide. We were especially interested in this compound because Schneider and Shohan,[1] working with a symmetrical xylenol prepared by synthesis, found that their specimen melted at 111° whereas Schiitz and collaborators,[2] Steinkopf and Höpner,[3] and Briickner[4] state that its melting point is 85 or 86°. We find this discrepancy to be explained by the fact that the material reported melting at 86° is a monohydrate, the anhydrous substance melting at 111°.

The xylenol which we used was a coal tar product melting at 63.2°, obtained from the U. S. Bureau of Mines. The hydrate of 1,3,5-xylenoxyacetic acid, easily prepared by crystallizing the product from water, melts actually at 81.0°, but is unstable, losing its water of crystallization on standing for a few days over phosphorus pentoxide in a vacuum desiccator at room temperature. The product then melts at 111.2'. A mixture of equal parts of hydrate and anhydrous material melted indistinctly between 97 and 104°. The hydrate loses at least a part of its water when it is dissolved in warm benzene and is reprecipitated by addition of petroleum ether. Schneider and Shohan reported 86–92° as the melting range of their product before recrystallization; they then recrystallized from benzene and found the melting point to be 111°. It is probable that their first product was largely the hydrate and that it lost water when warmed with benzene.

We report the melting point of the hydrate as 81.0° on the basis of the following evidence. The crude reaction product, isolated from aqueous alkaline medium by precipitation with hydrochloric acid, melted at 81–83°. We recrystallized it from water, and allowed it to stand in a desiccator

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(1) Schneider and Shohan, *Bur. Mines, Repts. Investigations No.* 2969, 1929, 10 pp.

(2) Schütz and co-workers, *Ber.*, **56**, 1971 (1923).

(3) Steinkopf and Höpner, *J. prakt. Chem.*, [2] *113*, 141 (1926).

(4) Brückner, *Erdöl und Ten*, 4, 562, 580, 598 (1928); *C. A.*, 23, 1246 (1929); *Z. Angcw. Chcm.*, 41, 1043, 1062 (1928).

in an atmosphere saturated with water vapor at room temperature, until weight equilibrium was reached. It then melted sharply at 81.0° corr. when heated at the usual rate of 1–2" per minute. The value 85 or 86° probably corresponds to a partially dehydrated product; for, if the temperature of the bath be raised very slowly, about 1° in three minutes, the hydrated substance will begin to melt at 81°, but at the same time will gradually become dehydrated; with cautious heating it is possible to reach 111°, the melting point of the anhydrous material, before fusion is complete; but it is also possible with irregular heating to observe melting at almost any point intermediate between 81 and 111°.

The solubility of the anhydrous substance in boiling water is about 1 g. in 100 cc.; in benzene, somewhat more than 1 g. in 10 cc.

Another property of 1,3,5-xylenoxyacetic acid not mentioned in the literature is its volatility in a current of steam. We found that 100 g. of steam in the course of one hour carried over 0.0066 g. weighed as anhydride.

Analysis.—A determination of water of crystallization was made in *a* micro vacuum drying tube over phosphorus pentoxide at about 70°: weight of sample, 4.395 mg.: H_2O found, 0.395 mg. or 8.99%; calcd. for $C_{10}H_{12}O_3.H_2O$, 9.09%. Micro combustion analysis of the anhydrous material remaining after the water determination gave the following results: weight of sample, 4.000 mg.: CO_2, 9.81 mg.; H_2O, 2.43 mg. C found, 66.88%; calcd., 66.63%; H found, 6.82%; calcd., 6.72%. This microanalysis was made by Mr. F. C. Silbert of this Laboratory.

COAL RESEARCH LABORATORY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA

RECEIVED JANUARY 11, 1933
PUBLISHED APRIL 6, 1933

Rotenone in a Species of Spatholobus

BY HOWARD A. JONES

Some time ago the Insecticide Division received a sample of roots[1] of a fish-poisoning plant from Burma, which the Economic Botanist of that country considered to be *Spatholobus roxburghii* Benth., a large, woody climber. In the course of tests of numerous plant extracts, Drake and Spies[2] found that an acetone extract of this root material possessed a high toxicity to goldfish. Recent tests by F. L. Campbell of the Bureau of Entomology also indicate that the extract is highly toxic to mosquito larvae.

While testing a number of plant extracts of high fish and insect toxicity for rotenone by the blue color test recently outlined,[3] the author found that the acetone extract of S. *roxburghii* gave a deep blue color, estimated to be

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(1) The material received consisted mainly of the bark of the root.

(2) Drake and Spies, J. *Econ. Entomol.*, **25**, 129 (1932).

(3) Jones and Smith, *Ind. Eng. Chem*, *Anal. Ed.*, **5**, 76 (1933).

equivalent to at least 1% rotenone or deguelin (both give the test). No further plant material was available. The remainder of the acetone extract, representing 6.3 g. of original material, was evaporated to dryness in a vacuum and the rotenone determined by crystallization from carbon tetrachloride.[4] The amount of material so obtained corresponded to about 1% of rotenone in the original root. This material recrystallized from absolute alcohol gave large, hexagonal plates melting at 163°, with indices of refraction identical with those of pure rotenone.

There are numerous species of Spatholobus, most of them native to India, the Malay Peninsula or the Philippine Islands. Since rotenone has now been found in *S. roxburghii* it would be well for investigators in these countries to study the rotenone content of plants of this genus.

[4] Jones, *Ind. Eng. Chem., Anal. Ed*., **5**, 23 (1933).

INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

RECEIVED JANUARY 12, 1933
PUBLISHED APRIL 6, 1933

COMMUNICATIONS TO THE EDITOR

THE ADSORPTION OF NITROGEN BY IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

The experimental work of recent years upon the mechanism of ammonia synthesis over iron catalysts has culminated in the idea that the synthesis occurs through nitrogen molecules reacting with the surface atoms of the iron catalyst to form a layer of nitrogen held to the surface by activated adsorption [see Taylor, THIS JOURNAL 53, 578 (1931)] or a surface iron nitride [see Frankenburger, Ullmann's "Enzyklopadic der technischen Chemie," 1928; Emmett, J. Chem. *Ed*., **7**, 2571 (1930)] which in turn can be reduced by hydrogen to form ammonia. Various indirect lines of evidence have been advanced in support of this hypothesis. However, as yet no data have been published to show whether the adsorption of nitrogen by the surface of an iron catalyst at synthesis temperatures proceeds at a sufficient rate to permit it to be an essential step in the synthesis of ammonia. The present letter presents briefly the results that have been obtained recently relative to the rate and extent of nitrogen adsorption by various types of iron ammonia catalysts.

At 400° and one atmosphere pressure 10-cc. samples of doubly promoted iron catalyst 931 containing 1.3% Al_2O_3 and 1.59% K_2O, pure iron catalyst 973, and singly promoted catalyst 921 containing 1.31% Al_2O_3 adsorbed

2.4, 0.26 and 6.3 cc. of nitrogen, respectively, in the first minute out of total adsorptions of 4.2, 0.93 and 8.2 cc. attained at the end of one to two hours These initial rates of adsorption are in approximately the same ratio as the rates of ammonia synthesis measured immediately after each adsorption run. Furthermore, the adsorption of nitrogen is sufficiently fast on each catalyst to permit it to constitute the first step in the synthesis of ammonia, in accordance with the hypothesis already advanced.

Measurements of the temperature coefficient of the rates of adsorption of nitrogen on catalyst 931 between 275 and 450° indicate an energy of activation of about 15,000 and 17,000 calories for the adsorption of 1.7 and 3.6 cc. of nitrogen, respectively. Isotherms at 400 and 450° correspond to a heat of adsorption between 34,000 and 40,000 calories. It appears therefore that the energy of activation of the desorption of nitrogen from the surface of the iron catalysts is between 49,000 and 57,000 calories. This seems to be in substantial agreement with the experiments of Winter [Z. *physik.* Chem., **B13,** 401 (1931)] in which he found that the temperature coefficient of ammonia decomposition over iron catalysts was about 54,000 calories and was apparently determined by the rate at which nitrogen was desorbed from the iron.

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
P. H. EMMETT
STEPHEN BRUNAUER

RECEIVED FEBRUARY 14, 1933 PUBLISHED APRIL 6, 1933

ENERGY OF ACTIVATION

Sir:

During the past two years, we[1] have extended our investigation of the kinetics of the ionic reactions (I) sodium bromoacetate + sodium thiosulfate, and (II) sodium β-bromopropionate + sodium thiosulfate, to determine the energy of activation, $E_{\text{act.}}$, and the constant B in the equation $\log k = B - E_{\text{act.}}/2.3\,RT$ as functions of temperature and concentration. The table illustrates some of the salient features.

TABLE

Reaction I. Na Bromoacetate (0.005 M) + $Na_2S_2O_3$ (0.005 M)

t, °C.	Added salt	$\sqrt{\mu}$	$E_{\text{act.}}$ Cal.	B (time unit minutes)
0–12.5	None	0.1414	16,062 ± 83	11.40
12.5–25	None	.1414	15,962 ± 68	11.28
25–37.5	None	.1414	15,849 ± 64	11.20
0–25	0.18 M NaCl	.447	15,960 ± 53	11.58
–25	.06 M $BaCl_2$	.447	16,299 ± 41	11.94
–25	.03 M $LaCl_3$	.447	17,695 ± 55	13.40

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(1) La Mer and Kamner, THIS JOURNAL, 63, 2832 (1931), for data at 25°.

TABLE (*Concluded*)

Reaction II. Na β-Bromopropionate + $Na_2S_2O_3$

t, °C.	Added salt	$\sqrt{\mu}$	$E_{\text{act.}}$ Cal.	B (time unit minutes)
$a = b = 0.005\ M$				
0–25	None	0.1414	28,900 ± 690	20.00
$a = b = 0.05\ M$				
0–12.5	None	.447	22,900 ± 150	
12.5–25.0	None	.447	24,400 ± 480	
0–25	None	.447	23,600 ± 220	15.5
$a = b = 0.005\ M$				
0–25	0.03 *M* $LaCl_3$	.447	24,000 ± 500	16.4
$a = b = 0.015\ M$				
0–25	0.0567 *M* $LaCl_3$	.633	22,000	14.5

$E_{\text{act.}}$ decreases with T for reaction I but increases for reaction II by an amount outside the probable error. That $E_{\text{act.}}$ may vary with T is not surprising since the partial molal heat capacities of ions are large negative[2] values, which are dependent upon the total charge, concentration, and specific properties; hence the heat capacity of the reactive complex need not be equal to the sum of the heat capacities of the reacting ions.

A study of the most reliable data on the reactions: (III) diacetone alcohol decomposition; (IV) sodium phenolate + various alkyl iodides in alcohol; (V) acetone dicarboxylic acid decomposition, furnishes evidence that our findings are not restricted to ionic reactions.[3,4,5] For reaction III, $E_{\text{act.}}$ (20–30°) = 17,040; E_{act} (25–35°) = 18,098, an increase which is eight times the experimental error. For reaction IV, using the ethyl iodide $E_{\text{act.}}$ (30.1–42.5°) = 21,067; (42.5–58.5°) = 21,604; (58.5–80.1) = 21,263. The increase in $E_{\text{act.}}$ at low temperatures followed by a decrease at higher temperatures is repeated uniformly by the eight primary alkyl iodides. The same behavior is indicated by reaction V.

The temperature dependence of $E_{\text{act.}}$ requires consideration of the following activation quantities: heat capacity $C_{\text{act.}}$; free energy $F_{\text{act.}}$; and entropy $S_{\text{act.}}$. Brönsted's equation for the influence of the medium follows readily in terms of $F_{\text{act.}}$; but the derivation in the light of R. C. Tolman's[6] statistical expression for $E_{\text{act.}}$ shows that in *general* f_X is a kinetic and not a pure thermodynamic activity coefficient. The collision number Z and the Arrhenius B are related by the equation $B = \log Z + S_{\text{act.}}/2.3\ R$. The simple collision theory consequently is valid only if $S_{\text{act.}} = 0$, which in turn requires the improbable assumption that $C_{\text{act.}}$ remains equal to zero down to absolute zero.

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(2) La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933); Randall and Rossini, *ibid.*, **51**, 323 (1929).

(3) G. M. Murphy, *ibid.*, **53**, 977 (1931).

(4) D. Segaller, *J. Chem. Soc.*, **105**, 106 (1914).

(5) E. O. Wiig, *J. Phys. Chem.*, **34**, 596 (1930).

(6) Tolman, "Statistical Mechanics," 1927, p. 261.

The importance of considering the entropy of activation is well illustrated by the $BaCl_2$ and $LaCl_3$ additions in Reaction I. In spite of an increase of 1800 calories in E_{act}, the velocity nevertheless increases due to an increase in $S_{act.}$ as shown by the marked increase in B.

Reaction III and the rearrangement of acetylchloroaminobenzene are being studied over wider ranges of temperature for a more convincing test of the conclusions drawn.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
VICTOR K. LA MER

RECEIVED FEBRUARY 17, 1933 PUBLISHED APRIL 6, 1933

MODIFICATION OF THE WILLARD–WINTER METHOD FOR FLUORINE DETERMINATION

Sir:

The use of standard thorium nitrate solutions for the titration of fluorine, as developed by Willard and Winter [*Ind. Eng. Chem.*, **Anal. Ed., 5, 7–10** (1933)], affords an accurate method for the determination of soluble fluorides. However, the end-point of the titration, when the amount of the zirconium–alizarin indicator specified by the writers is being used, is so faint as to be difficult to detect. Larger amounts of indicator cannot be employed, especially when one is titrating small quantities of fluorine, since zirconium combines with fluorine.

This difficulty can be avoided by the use of a 0.05% aqueous solution of sodium alizarin sulfonate alone as the indicator. The procedure is essentially the same as that employed by Willard and Winter. Three drops of the indicator solution are added to 40 cc. of solution containing 20 cc. of alcohol. Dilute hydrochloric acid (1:50) is added dropwise until the solution is colored yellow. A further drop of acid is then added. The end-point of the titration is recognized by the appearance of a faint, permanent pink color due to the formation of the thorium lake. The use of an arbitrary reference solution of the lake with a slight pink color makes for more accurate results, because the titrated solution shades from yellow to pink as the end-point is approached. The procedure succeeds best with fractional quantities of a milligram of fluorine, since the troublesome adsorption of the dye and lake on the precipitated thorium fluoride is rendered less noticeable.

The results tabulated below were obtained when solutions of sodium fluoride were titrated with a thorium nitrate solution of such strength that 1.0 cc. was equivalent to 0.2 mg. of the fluorine. The microburet readings were rounded off to the nearest 0.005 cc., and 0.030 cc. was subtracted from each of the readings to account for the thorium required to form the lake. The analyst did not know the fluorine content of the solutions marked with an asterisk,

$Th(NO_3)_4$, cc.	F Calcd., mg.	F Found, mg.	$Th(NO_3)_4$, cc.	F Calcd., mg.	F Found, mg.
0.260	0.050	0.052	0.990	0.200	0.198
.245		.049	1.020		.204
.520	.100	.104	1.000	.201*	.200
.505		.101	1.155	.230*	.231
.760	.150	.152	1.490	.300	.298
.865	.175*	.173	2.000	.400	.400

LABORATORY OF PHYSIOLOGICAL CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
W. D. ARMSTRONG

RECEIVED MARCH 8, 1933 PUBLISHED APRIL 6, 1933

A NEW BAND IN THE WATER VAPOR DISCHARGE

Sir:

In a spectrographic study of the electrodeless discharge in water vapor the writers have observed a band of moderate intensity with a head of wave length 3564 Å. This band is degraded toward the red and appears to have the structure of a hydride. It does not belong to any known system of hydroxyl bands and may prove to be due to OH^+. Other fainter bands were also observed which have not been measured accurately or identified. The analysis of these bands is being carried out under the direction of Professor F. W. Loomis of the Department of Physics.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
W. H. RODEBUSH
M. H. WAHL

RECEIVED MARCH 20, 1933 PUBLISHED APRIL 6, 1933

NEW BOOKS

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, de Biologie et de Technologie. (Annual Tables of Constants (A T C) and Numerical Data, Chemical, Physical, Biological and Technological.) Published under the Patronage of the International Research Council and of the International Union of Chemistry. American Agents, McGraw-Hill Book Co., Inc., 330 West 42d St., New York, 1931–1932. Vol. VIII, 2 parts (1927–1928), 2706 pp. Vol. IX (1929), 1607 pp.; Index to Vol. IX, 124 pp. 22 × 28 cm. Price, cloth, Vol. VIII, $20.00; Vol. IX, $16.00.

With the appearance of Volume IX for 1929 and of Volume VIII in two parts covering 1927–1928, Dr. Marie and the International Committee have finally completed the Herculean task of bringing the Annual Tables up to date, after the serious interruption and delay incident to the World War. Volume IX was issued at the end of 1931, and its Index a few months later. This resumption of prompt publication is of great importance to the scientific world, and Dr. Marie and the Committee are to be congratulated on their success. Volume IX occupies a total of 1731 pages, many more than any of its predecessors, thus reflecting the great increase in the output of new data. Chapters have been added on the following subjects: Absorption Spectra; Photography; Geophysics; Radioactivity; Structure by X-Rays; and Explosions and Combustion of Gaseous Mixtures. The Index provided with this volume is a new feature and is certainly a great added convenience.

It should be emphasized that a knowledge of French is not necessary in the use of these Annual Tables. All headings, titles, names, explanatory statements and indeed everything except the numerals themselves are given both in English and in French.

These volumes constitute a further invaluable addition to any library of the exact sciences.

ARTHUR B. LAMB

Prout's Hypothesis. Papers by WILLIAM PROUT, M.D.. J. S. STAS and C. MARIGNAC. Published by the Alembic Club, Edinburgh. Reprint No. 20. Gurney and Jackson, 33 Paternoster Row, London, E. C. 4, England, 1932. 58 pp. 12.5 X 19 cm. Price, $0.65.

This little book may be recommended highly to all those interested in the development of chemistry as a science. The type is clear and the binding light but good.

Twenty-four pages are devoted to an historical introduction, author anonymous, which furnishes an excellent setting for the papers which follow. The question of Prout's priority in stating his hypothesis is adequately treated with quotations from contemporary literature. The brilliant forecasting by Sir William Crookes and C. Marignac of our modem explanations of the deviations of atomic weights from integral values is well presented, but "Obviously there is no room in this introduction for a detailed account of the rehabilitation of Prout's hypothesis as effected by these recent advances."

Two papers by Dr. Prout are reprinted from the Annals of Philosophy. They begin with the assumption that air represents a chemical combination of oxygen and nitrogen and a theoretical calculation of the density of hydrogen which comes within one-half of one per cent. of the truth. Then follow some naive atomic weight determinations and finally the famous hypothesis.

From a long paper on atomic weights by J. S. Stas, the small portion dealing with the historical and the theoretical aspects of the subject is translated. Stas concluded that Prout's "law" was a pure illusion, that there was question whether even the atomic weight of oxygen was exactly an integral multiple of that of hydrogen.

Finally there is translated a commentary on Stas' paper by C. Marignac. In it Marignac makes a clear statement of what is now known as the packing effect. These last two papers illustrate the impossibility of overthrowing a theory with simple experimental evidence. In fact this reprint might be subtitled, the triumph of theory over experiment.

C. H. GREENE

Introductory General Chemistry. By STUART R. BRINKLEY, Associate Professor of Chemistry, Yale University. The Macmillan Co., 60 Fifth Ave., New York, 1932. x + 565 pp. Illustrated. 14.5 × 22.5 cm. Price, $3.00.

The author of this excellent and very readable textbook has sought "to afford an insight into that method of thought known as the scientific method, which differentiates the civilization of today from all which have preceded it; to develop a basis for an understanding of the true significance of chemistry in the modern world; to coördinate the facts, laws and theories of chemistry in an orderly science; and to limit the amount of specific descriptive and theoretical material, and to arrange the order of the topics so that the student may grasp the major development of the subject without becoming lost in a maze of minor details." This objective is accomplished in a manner which should appeal to teacher and student alike. Theories are presented only after the experimental facts upon which they are based have been strongly emphasized. Detailed facts of minor importance have been reduced to an agreeable minimum while fundamental principles are given a large amount of attention. The scientific method is always held in the foreground.

Each chapter carries a group of questions which should serve as a fruitful and stimulating source of thought to the student. The lists of supplementary readings which appear at the end of each chapter have been carefully selected.

Although the entire text seems very excellent, the first ten chapters seemed to the reviewer to be particularly well done. After all, it would appear that the first few chapters really "make" or "break" an elementary textbook—in the first ten chapters of this text the author has, it seems, given a very understandable presentation of the fundamentals, the thorough appreciation of which is essential to a grasp of the material that follows.

C. H. SORUM

Introductory College Chemistry. An Elementary Course Developed Historically. By HORACE G. DEMING, Professor of Chemistry, University of Nebraska. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1933. xii + 590 pp. 158 figs. 14 X 22.5 cm. Price, $3.00.

Most, although not all, new textbooks in General Chemistry are new only in the sense that they reflect some new author's literary and pedagogical personality. The outstanding facts and fundamental principles that should be included in an introductory course are so generally recognized that they appear in all standard texts. However, the manner in which these facts and principles are presented, the amount of detail involved in their clarification and the degree to which their practical utility is emphasized, may differ markedly—and herein, it seems, lies the real distinctiveness of a new book.

"Introductory College Chemistry" by the author of the highly popular and widely used Deming's "General Chemistry" is new and distinctive. Carrying the stamp of excellence of the above-mentioned "General Chemistry" it is "simpler and easier, follows a different plan, has completely new exercises, and is written for readers who are less advanced and perhaps less interested in chemistry as a profession." An easy and graceful style combines with clearly presented and aptly illustrated general principles to make it both readable and teachable. Outstanding topics are first presented in simple form and then repeatedly referred to in later chapters, "developing each subject gradually by repetition and enlargement." The history of the development of many interesting phases of chemistry is interwoven in a fascinating manner.

The index is very complete; repeated cross references make for greater clarity of subject matter; an appendix of definitions summarizes important ideas; each chapter is concluded by a very complete and comprehensive list of reading references; each individual subject within a chapter is numbered, a detail which is particularly valuable in making assignments.

The outstanding feature of the book, however, is the large number of questions and exercises of a very original and unusual character which appear throughout and at the end of each chapter. "A great many details that textbooks commonly present as statements of fact, particularly concerning the applications of individual elements and compounds, are made to appear as questions to provoke thought." Such questions are of genuine value to the student in that they encourage him to learn to think, which, after all, is one of the primary aims in teaching chemistry.

C. H. SORUM

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. System Number 30, Barium. Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 390 pp. 17 X 25 cm. Price, to subscribers, Mk. 56: singly, Mk. 64.

This volume constitutes another important instalment of this encyclopedia of inorganic chemistry. Eight authors collaborated in its preparation. The relevant literature has been covered up to the first of April, 1932.

There is in this volume a wealth of information as to the history, occurrence, preparation and properties of barium and of its compounds with the non-metals and with the alkali and alkaline earth metals. One is impressed, in comparing this volume with the corresponding instalment of the previous edition, with the great increase that has taken place in the amount of physicochemical data relative to this element, particularly in the fields of radiation and crystallography.

ARTHUR B. LAMB

Tables of Cubic Crystal Structure of Elements and Compounds. By I. E. KNAGGS AND B. KARLIK. With a Section on Alloys by C. F. Elam. Adam Hilger, Ltd., London, 1932. 90 pp. 16.5 X 25 cm. Price 11/6d.

This is a comprehensive uncritical summary of cubic structures of over 500 elements and compounds, and of about 150 alloys, reported up to August, 1931. The material is listed alphabetically and in order of increasing parameter, with numerous references.

C. D. WEST

Il Polarografo, sua Teoria e Applicazioni. (The Polarograph, its Theory and Applications.) By GIOVANNI SEMERANO. Libreria Editrice A. Draghi, Padova, Italy, 1932. vii + 207 pp. 13 X 19.5 cm. L. 16.

Professor J. Heyrovský's successful application of the dropping mercury cathode to the determination of the deposition and reduction potentials of ions in the aqueous solutions of their salts has resulted in a very exhaustive series of investigations by himself and his co-workers of the uses of this electrode in diverse chemical and related problems. The progress of these investigations became particularly rapid with the invention by Heyrovskjr and Shikata in 1925 of the "polarograph"—an apparatus for the automatic recording on photographic paper of the current–voltage curves obtained with a dropping mercury cathode—an invention affording a great economy of time and at the same time eliminating the personal element from the work. The extensive development during the last ten years of the method and of the practical applications by Heyrovskjr and his school led to the accumulation of a rich bibliography devoted entirely to the polarographic investigations.

Semerano believes that the method has passed the preliminary period of theoretical preparation and has definitely entered the field of practical utilization. He presents in his little book the theory and applications of the polarographic method, the aim of the monograph being "to offer to those who desire to occupy themselves with research of this type the possibility of acquiring the necessary theoretical and practical fundamentals."

After a concise and clear cut introduction, a discussion of the current–voltage curves is given, followed by a detailed description of the apparatus and the method, and a thorough presentation of the theory of deposition and reduction of ions at the dropping mercury cathode and of the maxima in the polarization curves.

The rest of the book is devoted to the practical applications. Data are given on reduction and deposition of the following ions: hydrogen, alkali and alkaline earth metals, metals of the iron group, zinc and manganese group, tin, arsenic, antimony, bismuth, lead, cadmium, mercury, gold, silver, gallium, indium, thallium, uranium, etc. This is followed by a discussion, with some experimental data, of the reduction of organic substances, and of the uses of the polarograph in determining solubility and equilibrium constants, mineral analysis, determination of impurities, titration of dilute solutions, and determination of oxygen dissolved in aqueous solutions. Finally a few pages are concerned with the biological, physiological, and industrial applications, such as analyses of sugar solutions, fermenting liquors and petroleum fractions.

The book is almost entirely in the nature of a compilation, Semerano himself having contributed but little to the subject. It seems that in his enthusiasm the author rather overestimates the practical usefulness of the method, which is inherently limited to work with very small concentrations, and to a permissible error of ten per cent.

However, the book will undoubtedly prove of interest not only to electrochemists, but also to all those workers in the fields bordering on chemistry who make use of electrochemical methods in their research. A complete bibliography of "Polarographic" literature is appended.

A. W. BOLDYREFF

Physical Chemistry for Students of Biology and Medicine. By DAVID INGERSOLL HITCHCOCK, Ph.D., Associate Professor of Physiology in the Yale University School of Medicine. Charles C. Thomas, Publisher, **220** East Monroe St., Springfield, Illinois, **1932.** xi + **182** pp. **26** figs. 14 **5** × **23.5** cm. Price, ***$2.75.***

Many students of biology and medicine feel increasingly the need of some knowledge of physical chemistry. To be of the greatest benefit, such knowledge should come early in the student's scientific training, whether or not he plans to take a more advanced course in the subject later on. This book is intended especially for such students. It deals successively with the gas laws, the theory of solutions, the law of mass action, buffer action, galvanic cells and PH measurements, adsorption and the colloidal state, membrane equilibrium, reaction velocity and enzyme action, oxidation–reduction potentials, and (briefly) with the concepts of total energy and free energy. There is also a chapter on blood, setting forth the application of physico-chemical principles to this physiological system. The lucidity of the presentation is admirable throughout. As might be expected from the author, the treatment of membrane equilibrium is excellent, being decidedly the best presentation of this subject for elementary students of which the reviewer is aware The often confusing subject of oxidation–reduction potentials is also set forth with great clarity. Inevitably some mathematical relations are assumed and must be taken on faith by most of the readers to whom the book is addressed; but Dr. Hitchcock has reduced this element nearly to the minimum possible under the circumstances.

As the author states in his preface, "the selection of topics has been guided by their past application in biological work." In the reviewer's opinion, it would be desirable to take the student further afield, and familiarize him with concepts which are likely to achieve biological significance in the years to come. The elements of the electronic theory of valence; the elements of electrostatics, especially dielectric constants and dipole moments; the orientation of molecules at interfaces and in fields of force—such topics as these are of real and rapidly growing importance to the biologist. They all furnish admirable opportunities for demonstrating the relation between the structure of molecules and their physico-chemical behavior: a relation which the biologist should be led to appreciate as early as possible because of the breadth and unity which it can give to his thinking. To take one example among many: if the student has some conception of the electrostatic forces which cause substances like sodium chloride and the amino acids to dissolve readily in water and hardly at all in fatty solvents, it will help to illuminate his conception of the chemical organization of the cell. The fundamental concepts involved in such subjects as those here mentioned could, furthermore, be treated with primary emphasis on simple physical ideas, and with relatively little mathematical apparatus.

Such questionings should not obscure the great success with which Dr. Hitchcock has fulfilled the aims he set out to achieve. For that success the book is to be heartily commended, and it will be found of great value by many teachers and students.

JOHN T. EDSALL

Organic **Chemistry.** By G. **ALBERT** HILL, Professor of Organic Chemistry, Wesleyan University, and **LOUISE KELLEY,** Professor of Organic Cnemistry, Goucher College. P. Blakiston's Son and Co., **1012** Walnut St., Philadelphia, Pa., **1932.** viii + **564** pp. **14.5** × **22** cm. Price, $3.00.

The authors planned this book as a text for "an elementary but comprehensive, one-year course in organic chemistry." It should be an excellent text for this purpose, for it is both well planned and well written. Of the **535** pages of text, **324** pages are devoted to aliphatic compounds and **168** pages to aromatic compounds. In addition to this material there are chapters on terpenes and camphors, heterocyclic compounds, alkaloids and plant and animal substances. The latter chapter, although comprising only 22 pages, is a concise and highly instructive introduction to the chemistry of hormones, enzymes, sterols, vitamins, lignin, rubber and natural pigments.

Besides its general high quality, certain features of this book particularly impressed the reviewer. The first is the sustained emphasis on the experimental side of organic chemistry. The importance and control of side reactions are brought to the reader's attention early in the book by the statement, "some unsympathetic soul has remarked that organic chemistry is the chemistry of side reactions and by-products. This statement is at least spiced with truth; however, by adjusting conditions the organic chemist can frequently cause the desired reaction, of several possible, to predominate, and in this necessary battle of wits against matter lies part of the charm of organic chemistry." Thereafter the authors take especial care to stress the dependence of the course upon the conditions of reaction. The inclusion of many of the recent developments in theoretical and applied chemistry is another striking feature of the book. The use of van Alphen's explanation of the formation of ether, the formulation of the Beckmann rearrangement as a transmigration of groups and the relation of structure to solubility and reactivity are examples of the type of discussion that will delight the teacher, while such recent developments as chloroprene and duprene, extraction of bromine from sea water, and the connection of tri-o-cresyl phosphate with Jamaica ginger paralysis should convince the student that organic chemistry is not a totally abstract science.

In addition to those mentioned above a few other features of the book may be noted, *viz.*, an introductory chapter on the historical background of organic chemistry, detailed discussions of the physiological action of many organic compounds, numerous tables listing the physical properties of members of various homologous series, and brief biographical notes concerning some of the contributors to organic chemistry.

Very few errors are to be found in the book. The incorrect formulas of quinine (p. **511)** and guaiacol (p. **527)** and the misstatement of the definition of saponification (p. **154)** are evidently oversights in proof reading. However, the assertion that aniline is the chief basic constituent "of coal tar (p. 363), the recommendation of acetyl chloride as a reagent for the separation of primary and secondary from tertiary amines (pp. **174,** 370), and the statement (p. **510)** that synthetic morphine is about to be produced commercially are examples of more fundamental errors and should be revised. These relatively few errors are the only faults which the reviewer can find in the book.

S. M. MCELVAIN

Laboratory Methods of Organic Chemistry. By L. GATTERMANN. Completely Revised by Heinrich Wieland. Translated from the Twenty-Second German Edition by W. McCartney. The Macmillan Company, 60 Fifth Ave., New York, 1932. xviii + 416 pp. Illustrated. 15 X 22.5 cm. Price, $3.50.

When, in 1894, Ludwig Gattermann prepared a modest manual to fulfill his private requirements in giving instruction in organic laboratory work, he probably little dreamed that the "cook book," as he called it, would be so widely circulated as to require up to the present time no less than twenty-two editions. One reason why "Gattermann" has remained a classic of the organic chemist for nearly forty years is that the plan of providing the preparative directions with theoretical explanations has proved very satisfactory. It is also evident from the wide use of the various German editions and the translations that the preparations originally included were well chosen and adequately described. A further factor contributing to the success of the book is that the author was widely recognized as an experimentalist of experience and distinction.

It is thus particularly appropriate that a thoroughly up-to-date revision of Gattermann's manual was undertaken by one of the outstanding leaders in the field of modern organic research, and it will be generally agreed that Wieland has performed a distinct service to the science by preparing one revision in 1925 and another in 1930. In doing so he wisely adhered to the plan of weaving into the practical directions an extensive survey of the theory of the reactions involved The re-writing and the amplifying of the theoretical parts of the book is indeed so well done that the new volume is not only a practical manual but serves also as an excellent and authoritative textbook of advanced organic chemistry. A knowledge of the principles of the subject being assumed, it is possible for the author to consider matters of theory in considerable detail and to cover a wide range of subjects in a volume which does not exceed a reasonable length. The book gains in importance in thus presenting Wieland's views and comments, particularly on the mechanisms of reactions.

The preparative directions also have been greatly improved and extended. Some idea of the novelty of the new preparations can be given by citing a few examples: experiments with triphenyl-methyl and diphenyl nitrogen, a synthesis of indigo, the extraction of nicotine, haemin and some of the bile acids; the saccharinification of potato starch, and the preparation of invertase from yeast. It will be evident that much of the new material has been chosen with a view to stimulating the student's interest in biochemistry, which in the author's opinion is "the most important branch of the subject." Throughout the descriptions of the various preparations and particularly in the chapters dealing with general laboratory operations, it is gratifying to find that the author has been careful to include some of the little devices and manipulative tricks which can add so much both to the success and the pleasure of laboratory work. The Nobel Prize laureaute does not hesitate, for example, to recommend new uses for old playing cards!

It should be pointed out that "Gattermann-Wieland," even though it is now available in translation, is hardly suitable for use in the courses of elementary organic chemistry given in this country. In the German universities the student takes up his work in the organic laboratory only after he has completed a course of lectures on the subject, and watched the lecturer perform numerous experiments. The American student, on the other hand, usually performs his first distillation a few days after attending his first lecture on the compounds of carbon. It is obvious that it is necessary to supply him with much more detailed directions than a book designed for the more mature German student can offer, and that he is not yet in a position to appreciate the wealth of information presented in the volume under discussion. It is in our advanced courses and courses of research that "Gattermann-Wieland" will be of greatest value, and every student who hopes to become an organic chemist should be encouraged to secure a copy as soon as he is able to use it intelligently.

The present translation requires little comment. For the most part it is accurate and clear, and, though the text lacks grace of expression, it must be declared adequate.

LOUIS F. FIESER

Alcohol and Man. The Effects of Alcohol on Man in Health and Disease. By HAVEN EMERSON, Editor. The Macmillan Company, 60 Fifth Ave., New York, 1932. 451 pp. Price, **$3.50.**

According to the preface, this book was compiled with the intention of placing before the general reader the accepted facts concerning the use and abuse of alcohol by man both in health and in disease.

Every effort has been made to avoid taking sides on the prohibition question. The work represents a painstaking effort to present the known facts and to show how these facts have come to be accepted.

In their effort to avoid taking sides, the editors appear to have leaned over backward and in many instances leave the reader in doubt as to the importance of many of the facts stated.

The chemists must be impressed with the uncertainty of many of the methods by which some of the facts have been determined. It would seem desirable to have a summary based upon logical conclusions from the facts as stated, with careful consideration given to the importance of these facts.

The whole work leaves one with the impression that the authors were uncertain as to the amount of weight which should be placed upon the results of some of the experimenters.

It would appear that the use of alcohol by those in good health was likely, if not certain, to result in diminished mental and muscular ability, that many of the popular beliefs were not founded upon facts and that in general a healthy person would be better in general health if alcohol was taboo. The same thing could easily be said about tea, coffee and many other articles in everyday use and probably facts determined by experiments could be adduced to prove the case.

After all is said and done, one who has read this book will very likely reach the conclusion that the matter is still in an experimental and uncertain stage, and that every one will be forced to decide for himself.

The toxic properties of alcohol in large doses appear to be accepted by everyone. The degree of toxicity between *ethyl* and *methyl* alcohol is left somewhat in doubt, for while *methyl* alcohol appears to be *less* poisonous so far as the immediate results of overdoses are concerned, most of the facts point toward more serious effects from continued small doses than is the case with ethyl alcohol.

The food value of ethyl alcohol appears to be quite definitely established within certain limits, but as each individual possesses specific peculiarities and as the conditions under which the alcohol is taken vary greatly, no really definite conclusion appears as to how much alcohol may be taken and used as food without unhappy results.

Taken all together, it is an interesting but indefinite book.

JOHN A. SEAVERNS

BOOKS RECEIVED

February 15, 1933–March 15, 1933

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E. Bauer. "Critique des Notions d'Éther, d'Éspace et de Temps. Cinématique de la Relativité." Hermann et Cie., fiditeurs, 6 Rue de la Sorbonne, Paris, France. **31** pp. Fr. 7.

L. Brillouin. "Notions de Mécanique Ondulatoire. Les Mkthods d'Approximations." Hermann et Cie., Éditeurs, **6** Rue de la Sorbonne, Paris, France. 34 p. Fr. 10.

Louis de Broglie. "Conséquences de la Relativité dans le Dkvelopment de la Mécanique Ondulatoire." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 15 pp. Fr. 6.

Élie Cart?. "Le Parallelisme Absolu et la Théorie Unitaire du Champ." Hermann et Cie., Editeurs, 6 Rue de la Sorbonne, Paris, France. 21 pp. Fr. 6.

G. Darmois. "La Théorie Einsteinienne de la Gravitation. Les Vérifications Expérimentales." Hermann et Cie., fiditeurs, 6 Rue de la Sorbonne, Paris, France. 30 pp. Fr. 7.

Clément Duval. "Manipulations de Chimie." Masson et Cie.. fiditeurs, 120 Boulevard Saint-Germain. Paris VI^{e}, France. 375 pp. Fr. 65.

J. Newton Friend. "A Textbook of Physical Chemistry." Vol. I. J. B. Lippincott Company, Philadelphia, Pa. 501 pp.

Paul Langevin. "La Relativité. Conclusion Generale." Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris. France. 17 pp. Fr. 6.

G. Masing. "Ternäre Systeme. Elementare Einfuhrung in die Theorie der Dreistofflegierungen." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 164 pp. M. 8.30; cardboard, M. 9.60

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Wilhelm Ziegelmayer. "Unsere Lebensmittel und ihre Veränderungen, mit einer Darstellung der Lehre von der Kochwissenschaft." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 322 pp. RM. 10; bound, RM. 11.20.

Edgard Zunz "Éléments de Pharmacodynamie Spéciale. Étude de l'Action des Divers Medicaments." Masson et Cie., Éditeurs, 120 Boulevard Saint-Germain, Paris VI", France. 2 Vols., 1272 pp. Fr. 190.

"A New Nomenclature of Chemistry, Proposed by Messrs. de Morveau, Lavoisier, Berthollet and Fourcroy; with Additions and Improvements by Lyman Spaldiig (1799)." Reprinted by the American Pharmaceutical Association, 10 West Chase St., Baltimore, Md. 12 pp. $1.00.